Annual Report 1978

Polymer Science and Standards Division

Center for Materials Science

POLYMER SCIENCE AND STANDARDS DIVISION

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In the 70 years since Baekeland introduced the first plastic produced entirely by the reaction of small molecules, plastics have left little of our culture and our technology untouched. We have moved rapidly into an age in which an overwhelming number of the needs of mankind are served by plastics.

From 1951 to 1976 the output of the plastics industry has grown by 11 percent per year, so that in 1976 over 22 teragrams of plastics were produced. This amounts to tens of billions of dollars worth of materials produced in hundreds of manufacturing plants by hundreds of thousands of workers. In addition to the domestic needs served, the polymer industry presently produces a two billion dollar favorable balance of trade.

Major trends in the use of plastics include increased use in packaging, in automobiles to reduce weight and improve fuel economy, and in medical implants. These increasingly sophisticated and demanding applications to which plastics are put has resulted in new needs for concepts, measurements, standards, and data that can be used to insure that plastics perform as intended not only in critical applications, but in processing and other phases of the materials cycle.

Major problems now being addressed include:

- A cooperative effort with the Bureau of Foods to produce methods of improved reliability for predicting both the rates of migration of small molecules from plastic containers into foodstuffs and the equilibrium concentrations that will be reached.

- Characterization of the surface properties of non-thrombogenic plastics and evaluation of the fatigue resistance of elastomers. Such materials are needed in efforts supported by the National Institutes of Health to develop artifical heart components and for improved circulatory assist devices.

- Improved polymer-based dental restorative materials and adhesives to make durable bonds between restorative materials and tooth tissue. This work involves extensive cooperation with the American Dental Association and the National Institute for Dental Research.

● The mechanical durability and permeation behavior of plastics used in containers for the safe transport of hazardous materials needed to insure reasonable regulation of such containers by the Office of Hazardous Materials of the Department of Transportation.

These problems and the others detailed in the following pages lead the scientists in the Division into a sophisticated and productive examination of those properties of polymers which must be contended with, often by people whose primary concern is non-technical, as our society increases its dependence on plastics.

Molecular weight and molecular weight distributions are the most important determinants of the useful properties of high polymers. They are of primary importance in determining both the processability of the raw materials and the characteristics of the fabricated products. Directly or indirectly, molecular weight is an important part of the specifications used in the commerce involving the tens of millions of tons of plastics produced every year. The ability to determine molecular weight reliably and reproducibly in different laboratories is thus important to both plastics producers and fabricators.

This task has four main technical activities, all aimed at this overall objective of providing a reliable base for the measurement system of molecular properties for use in commerce. First, the current needs of the measurement system used in industry are addressed by projects on the production of standards for molecular weight calibration and research on methods of improving the utilization of gel permeation or size exclusion chromatography which has become a widely used industrial measurement technique. The second technical activity provides the scientific basis for the molecular characterization methods of the future by exploring techniques and theories which meet needs we see growing in the plastics industry. One example of this is our projects concerned with block copolymers which are a rapidly growing segment of total plastics use. The third and fourth activities involve the development and application of molecular characterization methods to particularly critical plastics applications where market forces are not sufficient to attract sufficient industrial effort. Our present work in these activities relate to the use of ultra high molecular weight polyethylene for orthopedic implant use and the development and application of gas permeation measurement methods and standards.

Technical Activity

Polymeric Molecular Weight Standards

P. H. Verdier, H. L. Wagner, F. W. Wang, J. R. Maurey, R. E. Lowry

The principal methods used to estimate molecular weight, and in particular the only available method at present for estimating distribution in molecular weight, gel permeation chromatography, require the use of calibrants of known molecular weight. Hence the need for standards, which is being addressed by our production of a series of narrow molecular weight distribution polystyrene Standard Reference Materials with molecular weights which span the entire range of industrial interest. Polystyrene is important both in its own right, as a widely-used industrial plastic, and because molecular-weight measurements on other materials are often referred back to polystyrene by a variety of techniques.

In FY78 we have certified SRM 1478, a polystyrene with a weight-to-number average molecular weight ratio of 1.04. This SRM is certified for number-average molecular weight by membrane osmometry, weight-average molecular weight by sedimentation equilibrium ultracentrifugation, and limiting viscosity number in toluene at 25.0 °C by capillary viscometry. Analysis of the ultracentrifugation data utilized an automated procedure, recently developed at NBS and described elsewhere in this report, for "reading" the photographic plates which constitute the raw data of the experiment with an optical scanner and transmitting the data to a computer via magnetic tape. Use of this technique results in a 40% reduction in the labor costs associated with the ultracentrifugation work, which means a 20% reduction in the total cost of producing this SRM. The technique also clearly leads to an improvement in precision, but more experience will be needed to quantify it. The osmometry and viscometry work were carried out by conventional means. Careful experimental design and extensive replication were utilized to obtain results which define the current state of the art. This material will therefore be a useful molecular standard for some time to come.

During the current fiscal year, we have also carried out some preliminary studies on materials which are expected to become the next two members of our series of polystyrene molecular SRM's. These materials have molecular weights of less than ten thousand and nearly a million, and consequently some technical problems need to be solved in order to produce certificate-quality data. We will address these technical problems during the coming fiscal year and begin production in the latter half of FY79.

Automated Measurement of Interferograms from the Ultracentrifuge

F. W. Wang and F. L. McCrackin

Sedimentation equilibrium ultracentrifugation is a useful and versatile technique; it is capable of accurately determining the molecular weights of polymers over a range of molecular weights of several hundreds to tens of millions. Because the technique requires no calibration, it is especially useful for the characterization of polymer SRMs.

As commonly practiced, data from a sedimentation equilibrium experiment are in the form of a pattern of closely spaced interference fringes on a photographic plate containing the information relating concentration and radial position. The vertical displacement of an interference fringe between any two radial positions on the photographic plate is proportional to the concentration difference between the two positions. The manual measurement of these fringes is laborious and time consuming, even for a skilled operator.. Consequently, analyses are costly and only a small portion of the data available on the photographs is generally used.

We have developed an automated photographic plate analysis scheme utilizing a commercial image digitizer. The optical transmission of 20 micrometer square areas is recorded on magnetic tape. This tape is analyzed by a computer program to determine the interval and displacements of the fringes by a Fourier analysis of the transmission. The automated procedure was successfully used to measure the interference photographs from the sedimentation successfully used to measure the interference photographs from the sedimentation equilibrium experiments for determining the weight average molecular weight of SRM 1478 Polystyrene.

The chief advantage of the automated procedure is that it is much less laborious than manual methods. With the automated procedure, it is practical to measure routinely a much larger number of points than could reasonably be done by hand. A second advantage is that the automated procedure is capable of producing precise measuremsnts consistently and is less dependent than manual methods on the skill and experience of the operator. The automated procedure will be applied to the variable λ method in which the centrifugal force as well as the radial position is a variable. The variable λ method will determine both the number and weight average molecular weights of the polymers.

Recycle Size Exclusion Chromatography

F. L. McCrackin and H. L. Wagner

Recycle Size Exclusion Chromatography (SEC, formerly called GPC) was studied theoretically and experimentally as a method to measure the column spreading parameter and the polydispersity of nearly monodisperse polymer standards. The width of the recycled chromatograms were shown to be due for four causes; (1) the injection of the polymer in the column, (2) the column spreading, (3) the molecular weight distribution of the polymer and (4) spreading due to the pump. A method was developed to separate the sprading into contributions due to each of the individual causes. Previous analysis of recycle SEC considered the width of the chromatograms as due to only the column spreading and molecular weight distribution of the polymer. By taking the other contributions of the spreading of the chromatograpms into account, much more accurate values of the column spreading parameter and polydispersity of the polymer are obtained.

The recycle experiments were carried out with a set of micro-styragel columns of nominal pore size of 10^3, 10^4, 10^5 and 10^6 Å in a Waters 201 GPC system with a differential refractcmeter as a detector. The columns were calibrated in tetrahydrofuran and toluene with 5 narrow distribution anoinic polystyrenes ranging in molecular weight from 9000 to 498,000, including SRM 705 at 179,000.

SRM 1478 IN THE

7 POINTS RUN OF 3-17-78

TANGENT METHOD

$$\frac{\sigma^2_{CH}}{n}$$

CYCLES, n.
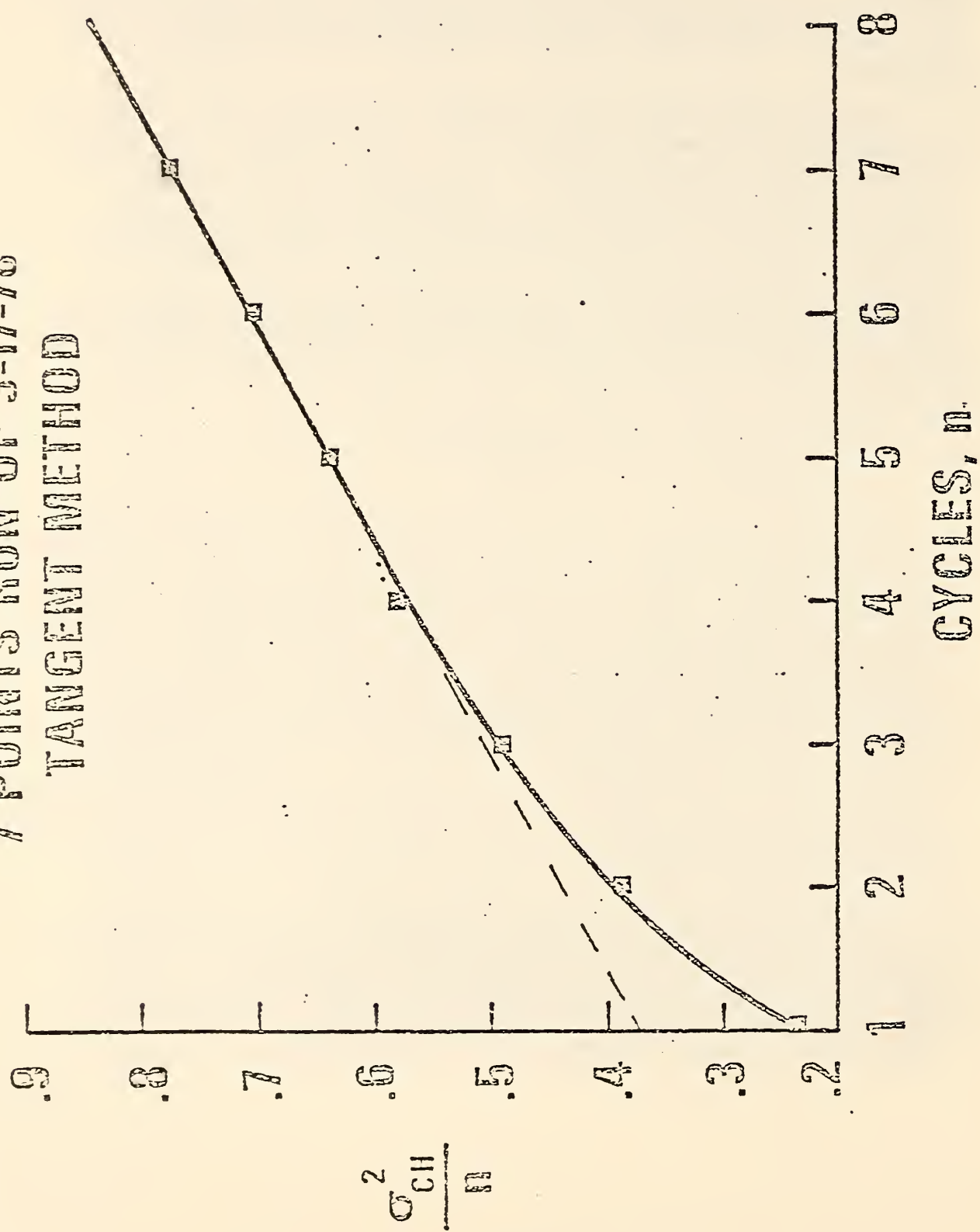
$$\frac{\sigma^2_{CH}}{n} = \frac{\sigma^2_I - \sigma^2_p}{n} + (\sigma^2_m + \sigma^2_c) + n(a^2 \ln M_w/M_n)$$

A typical result is shown in the figure for a polymer sample of 370,000 molecular weight in tetrahydrofuran. The square of the width of the chromatogram divided by the cycle number is plotted versus the cycle number. The solid line shows our fit to the data considering all four contributions to the width of the chromatograms, while the dashed straight line is the fit obtained by the two contributions previously considered.

The polydispersity, M_w/N_n, of one polystyrene polymer was measured to be 1.0034 and 1.0037 in tetrahydrofuran and toluene, respectively. Also the polydispersity of the polystyrene sample that is to be issued as SRM 1478 was measured to be 1.0078 and 1.0085 in tetrahydrofuran and toluene, respectively. A manuscript, including analysis of the skewness of the chromatograms, is being prepared.

Computer Programs to Analyze Size Exclusion Chromatographs

F. L. McCrackin

Many computer programs to analyze Size Exclusion Chromatographs (formerly called GPC) have been written. These have been combined and modified so that the programs will work on any computer that complies Fortran programs. A technical note is being prepared that will describe the programs and contain instructions for their use.

Solution Properties of Block and Graft Copolymers

F. W. Wang

The growing commercial use of block and graft copolymers makes it important to investigate whether the conventional solution properties techniques developed for homopolymers may be applied to block copolymers and graft copolymers. Previously, we have used the bead-spring model of Rouse and of Zimm to calculate the viscoelastic properties, the sedimentation coefficient, and the diffusion coefficient of block copolymers. The results of these calcualtions together with the experimental data of Prud'homme and coworker led us to propose a procedure for determining block-copolymer molecular weight from measurements of sedimentation coefficient (or translational diffusion coefficient) and limiting viscosity number.

Recently, we have calculated the dynamic flow birefringence and the flow dichroism of block-copolymer molecules in solution by modifying the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. The treatment considers the effects of the inhomogeneity in segmental optical properties as well as segmental frictional properties. The significance of the calculated results is twofold.[1] While difference in solution properties between homopolymers and block copolymers are often ascribed

to microphase separation, the results show that, even in the absence of microphase separation, the differences in optical properties of the dissimilar blocks may in some cases make the flow birefringence and flow dichroism of block copolymers strikingly different from those of homopolymers.[2] One may take advantage of teh results that the contributions of normal modes to flow birefringence and flow dichroism properties are weighted by generally different factors. For example, the determination of longer relaxation times may be·facilitated if, by manipulating block copolymer structure, the even normal modes are made to contribute very little to the flow bire-fringence or flow dichroism properties. Similar studies will be made on graft copolymers.

References:

1. . "Determination of Block-Copolymer Molecular Weight from Measure-ments of Frictional Properties," J. Polym. Sci: Polymer Symposium, 60, 201 (1977).
2. "Flow Birefringence and Flow Dichroism of Block-Copolymer Molecules in Solution," F. W. Wang, accepted for publication in Macromolecules, October 1978. ·

Dynamics of Polymer Chains

D. E. Kranbuehl and P. H. Verdier

The dynamical behavior of polymer chains is important for two reasons. First, the principal methods used to estimate molecular weight, and in particular gel permeation chromatography, the only method available at present for estimating distribution in molecular weight, are dynamical, non-equilibrium experiments which depend in part upon the relaxation of polymer chains in dilute solution. In its present state, the theory of these systems does not allow the calculation of molecular weight directly from measured quantities; a series of calibrants of known molecular weight is required. Improve-ments in the theory could reduce or even remove the need for calibrants, allowing the determination of molecular weight distribution of polymers for which calibrants are not available.

Second, the processability and the final characteristics of both plastics and elastomers depend in large part upon the relaxation behavior of the high-polymer chains of which these materials are primarily composed. More realistic theoretical treatments of polymer melts and elastomers, which must start with more realistic treatment of the dynamical behavior of the individual chains, will lead to more efficient processing and better fabricated end-products. A major shortcoming of present theory is its inability to treat chain entangle-ments in a realistic way. Our present work is aimed primarily at the study of entanglement effects, using a combination of analytical and computer simulation techniques. The simulation results provide data on

simple model systems and serve to guide the development of better theoretical treatments.

We have previously shown that for our simple chain models, entanglement effects lengthen the longest relaxation times of the chain by a factor proportional to about the first power of chain length. Recent theoretical work carried out elsewhere appears to predict a much weaker dependence of the lengthening of relaxation times upon chain length, which has led to the suggestion that our results are artifacts arising from special constraints in the very simple models we use. During the past year, we have obtained relaxation times for a series of somewhat less simple models free of these constraints, and have demonstrated that this suggestion is incorrect; at sufficiently large chain length the unconstrained chains behave in essentially the same way as the simpler, constrained chains. While carrying out this work, we have also discovered faster, hence more efficient, ways to carry out the simulations. This work is being written up for publication.

In the course of the simulation studies of relaxation behavior, equilibrium data are obtained as a byproduct. We have obtained distributions in the squares of a set of internal coordinates (Rouse coordinates). We earlier showed that the expansion of these coordinates by entanglement effects (which become the so-called excluded volume effects for equilibrium dimensions) is essentially a function only of the ratio of the chain length to the coordinate index. Examination of the distribution functions shows that with one exception, they are remarkably close to Gaussian. The one exception is the lowest Rouse coordinate, for which the distribution function exhibits the marked attrition at low values previously reproted by ourselves and others for the distribution in the square of end-to-end length. Taken together with our earlier studies of the relaxation behavior of these same Rouse coordinates, these results suggest that a relatively simple description of entanglement effects may be achieved in terms of Rouse coordinates, provided that the unique character of these effects upon the very lowest coordinates can be incorporated in a suitable way. These results are also being written up for publication.

Work planned for the coming year will proceed along three lines. First, there is at present an unresolved disagreement in the literature regarding the interpretation of the time-correlation functions obtained for flexible chain molecules in the quasi-elastic light scattering experiment. It is not clear whether these functions exhibit the entire spectrum of chain relaxation times or are dominated by the longest relaxation time. It appears that by direct simulation we may be able to resolve the disagreement, which will increase the value of measurements made by this relatively new technique. Second, a combination of analytical and simulation techniques will be employed in an attempt to relate the results of the simulation directly to

limiting viscosity number, widely employed as an indirect method for estimating molecular weight. Finally, as a first step in the direction of investigating melt properties, we will extend the simulation studies to non-dilute solutions.

Quasielastic Light Scattering

C. C. Han

Quasielastic light scattering provides a way to determine the dynamic properties of polymers without external perturbation except for the probing electro-magnetic waves. From measurements of the antular dependence of time correlation functions, molecular parameters such as molecular weight, persistance length, hydrodynamic radius, etc., can be obtained. Coupled with results obtainable from other scattering techniques, such as neutron scattering, this technique provides a powerful tool for polymer characterization. Two projects which have been pursued during the past year are described below:

Temperature and Molecular Weight Dependence of Polymer Chain Dimensions (with Z. Akcasu, Univ. of Michigan)

Theory has been developed and verified by experiments to explain the non-scaling behavior of the temperature and molecular weight dependence of polymer chain dimensions measured by different experimental techniques. Master curves can be produced to extrapolate as well as interpolate molecular weight from measured parameters such as radius of gyration or hydrodynamic radius. This will eliminate the ambiguity of relying on power laws (Mark-Houwink type) which are approximate and may only be used over narrow molecular weight and temperature ranges.

We are planning to extend this study to cover other hydro-dynamic measurement such as viscosity and also to cover stiff chain polymers. This kind of relationship between hydrodynamic variables and molecular weight provides a powerful technique in polymer characterization, especially to very high molecular weight polymers where extrapolation is necessary.

Molecular Weight and Polydispersity Determination (with F. L. McCrackin

The use of quasielastic light scattering measurements of molecular weight and polydispersity of polymers has been studied. Numerical procedures for comparison of experimental data with para-meterized molecular weight distribution functions has been developed. It has been demonstrated in the measurement of NBS SRM 706 polystyrene that this technique can provide fast and precise molecular weight measurements and also gives a quick but crude determination of M_w/M_n

ratio. Other advantages of this technique over the static light
scattering are insensitivity to dust interference and independence
from supplemental measurements such as dn/dc.

Small Angle Neutron Scattering

C. C. Han, B. Mozer, J. Hinkley & H. Yu, Univ. of Wisconsin)

Small angle neutron scattering (SANS) has been recognized in the
past few years as an important method for determining microscopic
aspects of material parameters. It has been very popular and extremely
successful in Europe in their application to materials research. NBS
has the only currently operating SANS facility in the U.S. and we
have been successful by pursued programs on molecular characterization
of block copolymers and on the measurement of molecular deformation
of strained rubber networks.

We are currently continuing work on different rubbery materials
by trying to correlate SANS data with mechanical and other dynamical
properties in order to increase basic understanding of this important
class of material. We have collaborated on this program with a group
from University of Wisconsin and more recently with French polymer
groups from CEN Saclay and CNRS Strasbourg. Several papers and invited
talks have been generated from this program and the potential of the
NBS SANS facility has been internationally recognized.

Technical Activity

The use of synthetic implants, man-made replacements for body
parts, is becoming more widespread every year. Currently 130,000
implants of Ultra-High Molecular Weight Polyethylene (UHMWPE) are used
annually for a wide variety of load bearing orthopedic prostheses
such as hip and knee joints. This is increasing not only because of
our growing elderly population but also because such surgery is being
performed more frequently on younger people as the outlook for long
term success becomes brighter.

These prostheses require resistance to creep and stress cracking
as well as the superior wear properties found in UHMWPE. The work on
this project has been concerned with the molecular characterization,
the fine structure, and the viscoelastic properties of UHMWPE.

The two main objectives of this project are: (a) the development
of new or modified standard methods for characterizing the molecular
weight and molecular weight distribution of UHMWPE. These methods
will provide industry with a needed capability for monitoring rigorously
the raw UHMWPE used in the manufacture of orthopaedic implants. This
capability is necessary since the above mentioned molecular parameters
strongly influence both the processing conditions used in the manu-
facture of the implants, as well as the physical properties (wear,

creep, stress cracking) of the products. They will also provide a basis for issuing an NBS SRM for the calibration of instruments used for characterizing the molecular parameters of UHMWPE. (b) The study of relevant aspects of the crystallization and morphology of UHMWPE in order to establish correlations between the molecular characteristics of the polymer, its fine structure, and its physical properties. Using such correlations as a basis, relevant criteria or guidelines can be established concerning the manufacture of implants possessing optimum physical properties for the intended end use.

Because many of the desirable properties of UHMWPE are due to its ver high molecular weight, the reliable determination of this quantity or the limiting fiscosity number from which the molecular weight may be obtained indirectly, as well as the molecular weight distribution, would be advantageous for optimizing these properties.

Previous work has established that single point dilute solution viscosity estimates of the molecular weight of UHMWPE, the basis on which the material is sold, are inaccurate. This is due primarily to the previously unrecognized shear rate dependence of the viscosity determination, and the lack of a valid relationship between molecular weight and viscosity (Mark-Houwink relation) for these very high molecular weight materials.

Low Shear Viscometer

J. Dillon and H. Wagner

In order to provide a meaningful characterization of UHMWPE it is first necessary to determine the limiting viscosity number in the limit of zero shear rate. The zero shear viscosity, an unambiguous quantity, can be the foundation of a rapid and convenient test method at finite rates of shear by polymer producers and implant fabricators alike.

For this purpose a low shear rotating cylinder fiscometer of the Zimm-Crothers type has been built. In this variation of this viscometer the shear stress is fixed by magnetic interaction of external electromagnets with an inner cylinder, causing it to rotate. The liquid being measured is kept between the fixed outer cylinder and the inner rotating cylinder which is suspended in the liquid. The rate of rotation is measured by a counter-timer developed in this laboratory by Dr. Charles Han. The viscometer is suspended in an oil bath at 135 °C.

The instrument is now being evaluated and checked for reliability.

Experiments aimed at determining the origins of the ill-defined lateral habits of teh lamellar crystals formed at 105 °C - 110 °C are underway. It is anticipated that these experiments will provide insights which are also relevant to the elucidation of aspects of chain folded crystallization in UHMWPE when it is crystallized from the melt.

Molecular Weight Determination of Ultra-High Molecular Weight (UHMW) Polymers by Static Light Scattering

J. R. Maurey and C. Han

Due to the need for high- and ultra-high molecular weight polymers in synthetic implant and other industrial applications, programs for characterizing implant materials and producing high molecular weight polystyrene Standard Reference Material has been under way. In this part of the program, determination of molecular weight will be carried out by static light scattering from polymer solutions.

A state-of-the-art light scattering photometer which is capable of measuring weight average molecular weight of UHMW polymers with precision, has been designed, fabricated and ready to be assembled and tested. This photometer is designed to utilize digital lock-in and photo detection techniques to provide high precision and large angular range needed to UHMW polymer measurement.

A differential refractometer is also under modification in order to provide the supplemental dn/dc value for light scattering measurement.

ASTM Activities

H. L. Wagner

Section D20.70.05 Molecular Weight Parameters: This section is charged with developing methods for the molecular characterization of polymers, and has concerned itself with writing recommended practices for determining molecular weight by various techniques other than by liquid size exclusion chromatography, (a function of D20.70.04). This year a method of determining number average molecular weight by osmotic pressure has been brought through D20 approval and is awaiting balloting by the entire Society. A method for determining weight average molecular weight by light scattering has been written and is being reviewed by a task force.

Section D20.70.04 Liquid Size Exclusion Chromatography: This section is charged with developing methods of measuring molecular weight and molecular weight distribution by liquid size exlcusion chromatography. Some of the topics currently under discussion are: Universal Calibration, Base Line problems, copolymers, branching and high

temperature methods. H. L. Wagner has written a high temperature addendum for the polystyrene method which will be considered at the forthcoming meeting of the task force in Miami.

. Technical Activity

Standards for Gas Transmission Rate Measurements

J. D. Barnes

The Polymer Science and Standards Division has been working closely with ASTM Committees F-2 on Flexible Barrier Materials and D-20 on Plastics to improve measurements of the gas transmission rate of plastic films, particularly those used in packaging of foods and drugs. The barrier properties of these films are a primary determinant of their effectiveness as media for safe and wholesome packaging. The existing test methodology is, for the most part, outmoded with respect to improved materials which are currently being developed. The Division has made .two substantial contributions to this area: (1) a polyester film has been certified as a Standard Reference Material for Oxygen Gas Transmission Rate (SRM 1470) and (2) a state-of-the-art automated manometric permeation measuring facility was developed and used to certify the values of SRM 1470.

FY 1978 saw an extensive effort put into documenting these achievements. We have also provided assistance to an ASTM task troup which is developing a new test method based on a coulometric detector for oxygen. We are continuing efforts to make SRM 1470 more useful to the measurement vommunity. We have examined film thickness and polymer density as potential sources of the unexpectedly large specimen-to-specimen variability which we encountered in characterizing the film originally. We expect to undertake studies to evaluate the long-term stability of the SRM under storage conditions. We have made preliminary measurements of the transmission rate of N_2 and CO_2 through SRM 1470 and we have proposed to complete this work in FY 1979. The manometric technique is the best one currently available for these latter gases.

Our automated manometric permeation measuring facility is currently being upgraded to provide better temperature stability and improved sensitivity. In addition to improved characterization of SRM 1470 this facility is expected to be useful in certifying SRMs whose barrier properties are better than those of SRM 1470. Candidate materials for such SRMs are currently under investigation. The barrier properties of these materials will be evaluated as soon as the new measuring facility is complete. Needs for other SRMs are continually being assessed as part of our involvement with the ASTM.

A number of applications of barrier materials involve more than one gas. We are seeking funding for measurements to determine mutual diffusion properties of O_2 and N_2, O_2 and H_2O and CO_2 with O_2 or N_2. This work will necessitate development of instrumentation to monitor permeation fluxes of two or more species simultaneously.

Improved Materials for Dissolved Oxygen Measuring Systems

J. D. Barnes

The Office of Ocean Engineering of the National Oceanic and Atmospheric Administration has sought technical assistance from the HBS Polymer Science and Standards Division in improving the accuracy and precision of dissolved oxygen (DO) measuring systems using membrane-type polarographic sensors. This undertaking was intiated late in the fiscal year and we are in the early stages of the work. The DO level is an important parameter in oceanographic and limnological studies. Low levels of DO indicate that sewage treatment plants are operating improperly. The presently available DO measuring systems are as varied as the needs they respond to. The development of these isntruments has proceeded with minimal input from theory. Performance evaluation has emphasized the system as a whole and there has been little emphasis on the effects of varying individual parameters. In this context the behavior of the membrane which is used to separate the electrolyte in which the working electrode and the reference electrode are embedded from the external medium whose oxygen tension is to be meausred is poorly understood.

When the system performance is viewed as a whole it is apparant that there are long term drifts in sensitivity which necessitate frequent recalibration. This performance may be tolerable in some applications but is is unacceptable in oceanographic applications, where the sensor must be unattended for long periods of time. As the first step in solving this problem we are modelling the diffusive transport of oxygen in the electrode system mathematically. This modelling has already shown that the transport properties of both the electrolyte layer and the membrane influence the sensitivity and the transient response of the electrode. It is generally thought that the contribution of the polymer membrane is dominant. In order to test this assertion we must identify the polymers which are being used. Our mathematical models have demonstrated how to combine the materials properties of teh electrolyte layer and the membrane to predict the transient response and the sensitivity. We will need to measure the permeability and the time-lag of teh important polymers in order to compare predicted with observed behavior.

Once the importance of the polymer in determining electrode sensitivity and transient response are identified we can proceed to look for effects which can change the diffusion field of the electrode to give the observed drifts. There are three effects which we

consider to be primary candidates: (1) compositional or geometric changes in the electrolyte layer, (2) stress relaxation effects in the membrane layer, and (3) solvation or plasticization effects in the membrane layer. It should be possible to examine these effects in a measuring system which is better defined than the polarographic electrode. Instrumentation developed in conjunction with our Standard Reference Material activiteis will be adapted to this purpose.

We are also going to examine membrane mateqials in addition to those currently in use in the hope of finding membranes with better transmission properties and better mechanical stability.

Viscosity Standards for Polymer Solutions

L. J. Zapas and J. S. Colton

Three distinct properties are necessary for the description of viscometric flows of non-newtonian systems, such as polymer melts and polymer solutions. The viscosity, first normal stress difference and the second normal stress difference, all as a function of rate of shear. In our standard samples we produced data only for the first two quantities. Preparing for the possibility of adding the second normal stress data, we obtained data on a 19.3% solution of poly-isobutylene (Vistanex L-100) in Cetane. We obtained reliable data on the first and second normal stress difference at a function of time and strain from single step stress relaxation experiments. The magnitude of the second normal stress difference is approximately one third of the first normal stress difference, though negative in sign at the low values of strain. The second normal stress difference is much more non-linear than the first. We were also able to obtain these quantities at relatively low rates of shear and the results are in agreement with previous data obtained in our laboratory by Dr. Kearsley.

Our results are new and show another way of evaluating the second normal stress difference which can be obtained from single step stress relaxation experiments.

Predictive Models for Polymer Performance

Research activities are focused on the development of theoretical models to predict the effects of molecule-molecule interactions on steady-state chemical kinetics and on the use of solid state NMR to elucidate the mechanisms of flame retardant action. The general subject of the effect of interactions between chemical systems on steady state kinetics has application to enzymatic processes in which enzyme-enzyme interactions may influence steady state enzyme kinetics. For example, the effect of protein-protein interactions on transport properties of cell membranes may be modeled.

The mechanisms of flame retardation is often poorly understood. A fundamental question is whether retardation occurs in the gas phase during burning or in the solid phase as a result of solid state chemical reactions. An improved understanding of the nature of flame retardant action should lead to the design and use of more effective flame retardants.

Technical Activity

Solid State NMR of Flame Retardant Polymer Systems

D. L. VanderHart, S. J. Kryder and W. Earl (NBS-NRC Postdoctoral Research Associate, Center for Fire Research, NEL).

Phosphorus containing compounds (such as $(NH_3)_3PO_4$) are in wide use as flame retardants for fabrics and plastics. The mechanism of flame retardant action is often poorly understood. A fundamental question is whether the retardation occurs in the gas phase during burning or in the solid phase as a result of solid state chemical reactions. For example, the current view of flame retardation in cellulosics which are of great commercial importance, especially in the building and fabrics industries, is that chemical reactions occur in the solid state to change the degradation pathway of cellulose so that water is given off and a char formed rather than evolution of volatile combustibles. The objectives of this project are to evaluate the importance of solid state chemistry in flame retardant action and the stability of flame retardants when added to the polymer during processing. Successful completion of these objectives should improve current understanding of the action of flame retardants and lead to the design and use of more effective flame retardants.

Recently developed techniques for directly observing the NMR signals from low abundance nuclei (*i.e*, C-13 at natural abundance) offer promise for studying P-31 dispersed at low concentrations in a flame retardant system. The techniques work best when an abundant spin system such as protons is also present. The signal from the low abundance nuclei is enhanced by cross polarization from the protons and the linewidth narrowed during observation by applying strong resonance irradiation to to the protons, thus eliminating dipolar broadening. To remove line

Standard Reference Materials for Rubber and Rubber Compounding

G. W. Bullman and G. B. McKenna

Many of the procedures used by industry for quality control and
commercial specifications of rubber depend upon NBS standard reference
materials (SRMs) which are maintained by the Polymer Science and
Standards Division. The objectives of the project are to renew SRMs
as stocks are depleted and to produce new SRMs needed by industry for
process control and commercial specification of newer types of rubber
materials.

Due to the lower priority given industrial standard reference
materials a workshop was held at NBS on October 31, 1977, to elicit
industrial support for a research associate program aimed at assisting
the development of new SRMs. The workshop was attended by represen-
tatives of the Rubber Manufacturers' Association (RMA), the Inter-
national Institute of Synthetic Rubber Producers (IISRP) and _____
representatives of rubber-related industries including manufacturers
of rubber and rubber products as well as suppliers of rubber
compounding ingredients. Plans for identification and production of
future SRMs were discussed, including newer kinds of rubber and the
need for characterization at the molecular level.

It was the recommendation of the workshop that ASTM and NBS work
with representatives of the industrial trade associations to define
possible areas of industrial support in the SRM program. Discussions
have been held with ASTM Committee D11 which has recommended support
for the Industrial Research Associate Program at NBS. Further
discussions with representatives of the RMA and IISRP are planned.

The Butyl Rubber SRM was reissued in December 1977 and current
plans are to reissue this extremely popular SRM again during the
coming fiscal year. In addition, a cross-linking agent used in the
vulcanization of rubber will be reissued.

A survey of rubber producers and users during the previous fiscal
year identified two additional rubber materials for which the industry
would like standard materials. One of these, EPDM elastomer, was
examined for storage stability and homogeneity during the past year.
Accelerated testing indicated that several EPDM elastmers were suitable
for use as standard materials.

broadening arising from chemical shift anisotropy sample spinning at a specific angle with respect to the magnetic field is employed. The combination of these techniques allows one to collect NMR spectra in solids at resolutions approaching those obtained in liquids. The power of high resolution solution NMR as an analytical tool for chemical identification is well established and it is a corresponding promise that guides this project in solids where materials subject to flames or pyrolysis may be analyzed in the solid state. The strengths of the method in comparisons with other techniques are that the results are quantitative, functionality of the resonating species can be identified, and insoluble substances or substances whose chemical stability might be questioned upon dissolution can be non-destructively analyzed.

Over the course of the past year the capability for doing C-13 NMR with sample spinning has been achieved. Greatly enhanced resolution has been observed in diverse intractable materials such as coal, sea sediments and cross-linked polymers using this method. The spinning probe for P-31 NMR is under construction and the next phase of the project will focus on verification of the mode of flame retardant action in cellulosics. This effort will primarily involve Dr. Earl and staff members from the Center for Fire Research.

Non-Equilibrium, Steady-State Behavior in a Driven System in Which Chemical Reactions Compete with Diffusion.

R. J. Rubin

The general subject of the effect of interactions between chemical systems on steady-state kinetics has application to enzymatic processes in which enzyme-enzyme interactions may influence steady-state enzyme kinetics. The particular forms of the interactions considered previously preserved the convenient property that population distributions at steady state have a quasi-equilibrium form. More general interacting two-state enzyme systems destroy the quasi-equilibrium form of the steady state. The objectives of the present project are to compare the properties of a more general interacting two-state system with the corresponding non-interacting system and to develop a method for solving explicitly a large system of linear steady-state rate equations in terms of the solution of the corresponding non-interacting enzyme system.

The approach follows analogous methods of solution which have been used successfully in analyzing a model exhibiting Brownian motion and a model of polymer chain absorption. A lattice-fluid model is used to treat the system of an interacting enzyme system that combines cyclic biochemical reactions with diffusion. The lattice consists of a one-dimensional ring which is not fully occupied by enzyme molecules and in which the molecules can diffuse to unfilled sites. Using this approach, it has been possible to compare the properties of a non-interacting system with those of the same system only in which more

general forms of enzyme-enzyme interactions are operative. Furthermore, it has been demonstrated that the methods used do allow one to solve explicitly a large system of linear steady-state rate equations in terms of the solution of the corresponding non-interacting system.

Test Methods for the Chemical Durability of Plastics in Use

The extensive use of polymeric materials in the replacement of
other materials and in the creation of new applcations has placed a
much greater importance on the study of their expected lifetimes.
This task on chemical durability focuses primarily on modes of failure
of plastics in non-loadbearing applications but the environmental
influences involved in thermal, oxidative, hydrolytic and photolytic
degradation strongly affect mechanical performance as well. The
objective of the task is the development of accurate test methods for
the measurement of polymer durability in use. This necessarily
involves investigation of the primary mechanisms of degradation as
well as analysis and rate measurements. The task is divided techni-
cally into three areas: Thermogravemetric methods; Thermals and
Hydrolytic Degradation of Polyurethane Elastomers; and Oxidative
Degradation.

The measurement of weight loss is a traditional technique for the
investigation of polymer degradation reactions. It is simple, conven-
ient, and, in some applications, fairly fast. It is applicable almost
to all polymeric materials, and modern gravimetric apparatuses are
rugged, stable, and accurate.   The processes which produce
small volatile fragments are often closely coupled kinetically to the
processes responsible for deterioration of plastics. Two unique
apparatuses for investigating the kinetics of weight loss have been
utilized during the past year. These new techniques have been applied
to several vinyl polymers, and the theory and philosphy of lifetime
prediction has been further developed.

Technical Activity

Error Propagation Analysis of Activation Energy Extrapolation

B. Dickens and J.H. Flynn

An analysis of the statistics of error propagation in the extra-
polation of activation energies obtained from accelerated conditions
to determine rates of deterioration at service conditions demonstrated
that either extremely accurate values for the activation energy are
necessary (error < 0.05 percent) or the range of temperature extrapo-
lation must be modest (< 100 °C) if the predictions are to have
usefully narrow limits of error. These conditions are not fulfilled
in traditional thermogravimetric techniques. The experimental tech-
niques described subsequently reflect an effort to conform to these
limitations.

Effects of Heating Rate Upon the Coupling of Complex Reactions

J. H. Flynn

Calculations were performed for the effects of shifts in heating rate on the rate of weight loss for two model cases: competitive and independent reactions. Processes with a 20 kcal/mole difference in activation energy are well resolved by shifts of 10^4 in heating rate. These shifts are realizable with our equipment. Often, several kinetic processes are in competition during the degradation of polymeric materials. Comparison of these changes with theoretical cases such as the above should give an insight into the mode of kinetic coupling of competing processes.

Factor Jump Thermogravimetry

B. Dickens and J. H. Flynn

This new technique which we have developed at NBS consists of imposing a series of temperature plateaus on a sample while recording its weight. The values for activation energy obtained by interpolation between successive plateaus are both independent of one another and sample history. The apparatus has been completely automated and computer control allows the determination of large numbers of values for activation energy. Averages of these values reach a precision for which extrapolation to service conditions is practical.

An investigation of the thermal and oxidative degradations of polystyrene has resulted in values of 44.9 ± 0.2 and 21.5 ± 0.2 kcal/mole for the respective thermal and oxidative activation energies. The value, 45, is in good agreement with values obtained by other techniques and is 10 kcal/mole lower than a value of 55 kcal/mole which is often quoted as the activation energy for polystyrene degradation. Similarly, precise measurements have been made for poly(methyl methacrylate), polyethylene and polypropylene, and the results have been prepared for publication.

The factor jump apparatus has the potential for much wider application, *e.g.*, quantitative determination of the effects on the rate of degradation of other factors such as water vapor, pressure, radiation, etc. However, the apparatus will not receive as high a level of use in the coming year as Dr. Dickens is on a training assignment as a NATO fellow at Le Centre de Recherche les Macromolecules (CRM) in Strasbourg, France.

Variable Heating Rate Thermogravimetry

J. H. Flynn

In the prediction of service life of polymers from accelerated
weight loss experiments, it is crucial to shorten the interval of
temperature extrapolation and to predict with some confidence which
of the often several compelling degradation processes will be dominant
as service temperatures. The kinetics of weight loss of several poly-
mers are being investigated on an apparatus which operates at heating
rates from 6 deg/min to 9 deg/day. The high sensitivity and baseline
stability of the apparatus permits measurement of the initial part of
the degradation. This is the region in which many polymers lose their
desirable properties. Experiments over the full range of conversion
and a wide range of temperatures permit an assessment of the kinetic
coupling of complex reactions. The experiments at very slow heating
rates reduced the temperature exptrapolation by over 100 ^oC in compar-
ison to typical thermogravimetric experiments.

The investigation of the thermal degradation of polystyrene
yielded an activation energy of 47.5 kcal/mole over the wide temperature
range of 280 to 420 ^oC, further weakening the case for the previously
accepted high value. Evidence for the presence of "weak links" was
found in the 200-250 ^oC temperature range from the experiments at
slowest heating rates. The thermal degradation of a poly(methyl
methacrylate) sample was found to involve at least four separate
reactions.

The continuance of these investigations, particularly looking
into the roles played by other factors such as oxygen and water vapor,
should lead to an assessment of the viability of weight loss measure-
ment for the prediction of service life of polymers.

These techniques have developed to a point where automation of
the apparatus for the more efficient and extensive collection of data
should be profitable.

Thermal Decomposition of Vinyl Polymers

R. E. Florin, C. Cascaval, S. Strauss and D. W. Brown

Polystyrene with end groups derived from azoisobutyronitrile was
shown to decompose by an end initiation mechanism much like thermally
prepared polystyrene and unlike anionic polystyrene.

Even at very high molecular weights of 5 million, poly(α-methyl-
styrene) follows the simple mechanism of random initiation and very
long zip length obeyed by samples of lower molecular weight. The
approach to limiting high molecular weight asymptotic behavior is

remarkably gradual, but this was shown by a transformation to be a consequence of the original kinetic equations. Experiments with large thicknesses at lower temperatures were inconsistent with the others, and exhibited a lower zip length.

Technical Activity

This project has for its object the determination of kinetic mechanism for the thermal and hydrolytic degradation of polyurethanes. The results are to be applicable to the estimation of aging characteristics and lifetime limits of polyurethane elastomers. It is sponsored by the Naval Air Systems Command and the Chemistry Program of the Office of Naval Research.

The emphasis this past year has been placed on the hydrolytic mechanisms of failure; however, work is continuing on the thermal and oxidative processes involved in the deterioration of polyurethanes.

Thermal and Oxidative Degradation of Polyurethanes

J. H. Flynn, B. Dickens, W. J. Pummer and L. E. Smith

A series of model urethanes, synthesized in our laboratory under controlled conditions, and several commercial samples have been thermally and oxidatively degraded using the techniques and apparatuses described in the previous sections. The philosophy of these techniques and their application to the interpretation of weight loss kinetics has also been previously described.

Both factor jump and constant heating rate thermogravimetry point up many differences in the decomposition processes between polyurethanes of differing disocyanate and soft segment composition. The investigation of initial rates of weight loss have shown that toluene disocyanate (TDI) polyurethanes are less thermally stable than corresponding methylene diphenyl disocyanate (MDI) polyurethanes. A prominant role of oxygen in the degradation of these polymers was found in the initial phases of weight loss at low temperatures. This effect was not evident at conventional accelerated test conditions where oxygen appeared to have little effect on the weight loss kinetics. Further effects of oxygen and effects of water vapor on the degradation of these polyurethanes will be investigated during the coming year.

Hydrolytic Degradation of Polyester Polyurethane Elastomers

D. W. Brown, R. E. Lowry and L. E. Smith

Polyester polyurethane elastomers are high-modulus rubbers with good resistance to hydrocarbon fuels. In warm humid environments they undergo reversion to viscous liquids. The chemistry of the reversion

is an acid-catalyzed hydrolysis of the polyester component [1,2]. Despite this understanding, there is an inability to predict lifetimes. Installations in military aircraft that were expected to last 10 years frequently have had to be replaced in 2 to 4 years at great expense [3]. The Polymer Division was asked by the Naval Air Systems Command to develop a method that would permit good prediction of lifetime from short term tests. The problem was not of great concern to industry because only a small fraction of the total polyester polyurethane production is involved. Sponsorship was later transferred to the Naval Ordinance Laboratory; some Bureau funds have also been committed.

Previous lifetime estimates for these materials have been based on changes in a physical property at 25 °C, such as tensile strength or modulus. We have found that as the polymers decrease in molecular weight on aging they also become more crystallizable; the extra crystallinity can augment the physical properties and may have led to the general overestimate of the lifetimes [4a, b].

It is felt that lifetimes will be properly predicted by the following procedure. Existing data on changes in acid content [2] appear to follow the relation

$$A = A_o e^{kt} \qquad (1)$$

where A is the acid content (initial value, A_o) t is time, and k is a pseudo first order rate constant. If each scission of the polymer chain creates one acid group then:

$$\frac{1}{M} - \frac{1}{M_o} = A - A_o = A_o (e^{kt} - 1) \text{ and } \frac{1}{M} = A_o e^{kt} - A_o + (1/M_o) \qquad (2)$$

where M is the number average molecular weight (initial value, M_o). By measuring the change in M or the change in A on aging one can calculate k. Since k is a chemical rate constant it should obey the Arhenius equation, permitting extrapolation to any desired temperature. We have aged three commercial polyester polyurethanes at 55 °C and measured A_o, M_o, and M. Fig. 1 is a plot of 1/M versus time. Symbols show the experimental data; the lines are calculated according to Eq. 2, using a value of k that forces a fit at the longest time for each polymer. Intermediate points fall close to the appropriate curves. More results are in prospect, both at 55 °C and at other temperatures.

Stress-strain measurements were made on some aged samples, both at 25 °C and at 70 °C. The latter temperature was used to try to eliminate the effect of the crystallinity caused by aging. Consistently, below an M of 10^4 there is an inability to withstand elongations of greater than 100% at 70 °C. At 25 °C specimens of the same aged material withstand 300% elongation, without much reduction in

stress compared with that of unaged samples. Therefore reduction to an M of 10^4 will be suggested as the criterion of failure. Using this, at 55 $^\circ$C the lifetimes of polymers A and C are about 155 days, while that of B is only 68 days.

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Measurement of Oxidative Degradation by Chemiluminescence

R. E. Florin and B. Dickens

Interest has recently risen in the use of chemiluminescence to monitor the oxidative deterioration of organic materials. Plastics, lubricants and other organic materials emit light weakly during slow oxidation. According to the simplest accepted explanation, this light is associated with the termination step of the oxidation chain reaction. Although the quantum efficiency of emission is very low, of the order of 10^{-9} photon per termination event, the use of photomultiplier tubes in the photon counting mode of operation results in a high overall sensitivity of detection. Even the very low rates of reaction occurring at temperatures near actual service temperatures are potentially detectable. Most other methods of measuring oxidation are accelerated tests run at high temperature, requiring a long and somewhat uncertain extrapolation downward to predict service behavior. However, the growing popularity of chemiluminescence would be on a firmer quantitative basis if (a) the mechanism were more firmly established to be as described and (b) the relation between the assumed termination step and the intermediate oxygen consuming steps, *i.e.*, the kinetic chain length, were known for a variety of typical examples. Some workers have evaded these difficulties with the "oxygen drop" method, in which only the volume of oxygen consumed and the time to cessation of luminescence are measured, but in this method the crucial measurements are the same as those used in customary methods and the advantage of high sensitivity is lost.

We are preparing to measure rate constants and ratios of rate constants in the oxidation chain reaction for typical rubbery and glassy polymers. Initially the effort will be concentrated on

measuring the termination rate. Of several possible methods, the one will be chosen in which a mixture of polymer, oxygen and photoinitiator is put into a photo-initiated steady state by the use of ultraviolet light. The light is then suddenly cut off and the decreasing intensity of chemiluminescent emission observed as a function of time. From plots involving the square root of intensity the value of the second-order termination rate constant can be deduced.

During the current year the shop has built the sample chamber carrying two electronic shutters, one for the ultraviolet source and one for the photomultiplier detector, and a safety interlock for the two shutters has been devised and constructed. Wiring has been set up to connect the shutter controls and data output to a MIDAS frame. Two alternative computer programs -- a Fortran and a slower BASIC version -- have been developed by B. Dickens and tested by B. Dickens and R. E. Florin for repetitive computer controlled experiments and data logging. Several polymer samples have been procured. It is planned to determine the termination rate constant for two rubbery and two glassy polymers at several temperatures during the coming year, and to expand the list subsequently. Results will be compared with electron spin resonance observations of peroxy free radical decay, at least in the glassy systems where decay is expected to be slow, and also compared with oxygen consumption rates at the higher temperatures. More complicated studies on heterogeneous systems, planned for later years include effects of morphology on oxidation rate in semi-crystalline polymers. The equipment is also adaptable to empirical studies of effects of inhibitors, and, with modifications, to monitoring oxidation initiated by mechanical stress.

Photophysical Processes in Polymers

F. W. Wang and R. E. Lowry

Photophysical processes in polymers are significant as the primary steps in photo-activated polymer degradation. Therefore, a knowledge of the effects of structure and mobility on photophysical processes in polymers will lead to a more efficient application of photo-phenomena in the polymer field. In addition, by labeling polymers with fluorescent groups, we may use some photophysical processes such as energy transfer and excimer formation to study intermolecular and intramolecular interactions in polymer solutions and polymer blends.

We have developed synthetic procedures for preparing acrylate and methacrylate polymers which carry fluorescent groups. These polymers will be used to study the role of molecular structure and mobility in polymer photophysics and to study the compatibility of polymers in solution and in blends.

Free Radicals in Stressed Polymers

R. E. Florin

A note was accepted for publication which demonstrated the
detection of free radicals in stressed vinylidene chloride copolymer
filaments by electron spin resonance, using chloranil as a radical
trap.

Tests, Standards and Characterization for Manufacturing and
Durability of Dental and Medical Materials

The objective of this research is to contribute to dental
health care through development of better performing materials and
test methodology and standards appropriate thereto. Materials re-
search and techniques are pursued with the goal of developing adhe-
sive composite restorative materials of greater durability and wear
resistance, and improved base metal alloy alternatives to the costly
gold alloy prostheses. Improved test methodology is sought for
characterization of the surfaces of surgical implant materials and
for defining the interactions that occur thereon.

Dental research directions in support of the objective are
established collaboratively with the American Dental Association,
the National Institute of Dental Research and the Department of
Defense Dental Services. Medical materials research is guided by
close interaction with the National Heart, Lung and Blood Institute
and the ASTM F4 Committee: Medical and Surgical Materials and
Devices.

Technical Activity

Resin Matrix Materials

*J. Antonucci, G. Brauer, J. Jackson, D. Dulik,
J. Peckoo and J. Cassel*

Early work in this laboratory resulted in the development of a
prototype resin system that was used by dental manufacturers as they
introduced composite restorative systems to dental practice. The
deficiencies in the resin system as developed by NBS and as currently
used by the industry are: an ill-defined color stability problem,
a high viscosity which requires dilution with lower viscosity, com-
patible monomers and insufficient storage stability except under
ideal conditions.

The approach has been to synthesize and characterize monomers
capable of *in situ* polymerization at room temperature within the
time limits practical for dentistry, with special emphasis placed on
monomers that can be achieved in high purity as one means of im-
proving color stability. Several resin systems derived by mixing
crystalline monomers in proper proportions to give sufficiently low
melting eutectics have not proven adequate in all aspects.

To form polymeric matrices with lower surface energies and to
reduce the polymerization shrinkage that contributes to poor marginal
adaptation and hence marginal leakage of the composite restoration

several directions are being explored. One is the use of fluorinated prepolymers as components of the resin formulation to reduce water absorption and polymerization shrinkage. Tensile strength of the composites derived have varied with the particular prepolymer prepared but the approach appears promising.

Marginal leakage experiments have been initiated to determine the contributing influence of various diluent monomers that might be used with Bis-GMA, the main resin component of today's commercial dental composite system.

Due to the relatively low half-life temperature of benzoyl peroxide, the initiator used in today's dental composites, the storage stability of the composite formulations can be a problem. The other component of today's commercial composite catalyst system is an aromatic tertiary amine which is considered a likely contributor to color instability in the system. We have demonstrated that it is possible to devise alternative initiator systems based on the use of more stable peroxides, such as organic hydroperoxides and peresters, and less color prone as well as more biocompatible accelerators such as ascorbic acid or its palmitate ester. The free radical decomposition of the more stable peroxides requires trace amounts of certain multivalent metals. Because so little redox metal is required, neither color nor toxicity problems should arise. Considerably more experimentation with this promising new catalyst system will be required.

We have also examined a wide range of amine accelerators with the aim of correlating structure and reactivity for the composite system. Tests such as hardening times, tensile and compressive strength and water absorption all as a function of amine accelerator concentration are carried out and we have been able to establish an approximate order of the accelerating ability of 15 potentially useful amines. Synergistic effects of one amine in the presence of another have been noted. The sensitivity of the compressive strength of a dental composite to the concentration of the amine accelerator has been clearly demonstrated, a maximum in the data being reached at about the 17 millimol concentration. A few more amines which we predict from structure-property relationships to be highly reactive are to be synthesized and evaluated for conclusion of this phase of the effort.

For a better understanding of the mechanism of the typical amine-peroxide reaction and a more firm basis on which to select amines, we have initiated an investigation of the ionization potentials of tertiary amines using ion cyclotron resonance spectroscopy as the investigative tool.

Development of Adhesive Bonding Techniques

G. M. Brauer, J. M. Antonucci, D. Dulik,
C. Hartranft, J. M. Cassel

A dentally applicable technique which established and main-
tained adhesive bonding would not only offer an important means for
reducing the dental caries that is encouraged by percolation of
fluids and bacteria at restoration margins but would afford a means
of changing the mode of cavity preparation so as to reduce the ex-
tent of sound tooth structure destruction. Strong mechanical bonding
of acrylic resins to enamel surfaces can be obtained through acid
etching of such surfaces but such treatment is not applicable to the
surfaces of dentin, the other major component of teeth.

An immediate objective has been to extend to longer periods the
promising short term adhesion obtained to dentin with 2-cyanoacry-
lates. Assuming that failure of the bonding over prolonged exposure
to water has been of a hydrolytic nature, we have (1) attempted mod-
ifications of the adhesive, *e.g.*, introduction of cross linking
agents, (2) use of a protective water-repellant film over the adhe-
sive and (3) pretreatments of the dentin surface with very dilute
organic acids as a means of more effectively removing debris from
the bonding area or with allyl compounds capable of copolymerization.
Judging by accelerated aging tests which incorporate thermocycling
between 5 °C and 60 °C, none of the above procedures which lead to
promising initial adhesion values produces the required level of long
term stability in the bonding. The most promising results have been
obtained with the dilute citric acid pretreatment.

We are initiating an examination of the use of urethane monomers
with residual isocyanates and with methacrylate groups as part of
the structure. Both aromatic and aliphatic type structures have been
synthesized and will be investigated for bonding to both bone and
dentin surfaces.

The bonding potential to bone or dentin of a methacrylate mono-
mer system containing free aldehydic groups for reaction with their
collagen components has not materialized, perhaps due to an inacces-
sibility of the collagen on the surface of these mineralized tissues.

We have shown that it is feasible to mordant dentin with low
concentrations of redox metals and these metal ions in their less
stable oxidation state serve as effective activators for the free
radical decomposition of hydroperoxides and peresters. With the
ascorbic acid-peroxide polymerization catalyst system it is feasible
that we can reduce attached metal ions to a lower valent state and
induce polymerization of a dental resin in an acceptable time. This
route to graft polymerization will be explored further.

Wear Resistance and Mechanical Properties

J. E. McKinney, J. M. Cassel

An immediate objective of this effort is to demonstrate that data can be obtained with an accelerated laboratory test that will predict the durability of composite restorative materials when they are used in stress bearing situations. Such a test procedure would eliminate the need for the very costly clinical trials that are now required. A second principal objective is to define the mechanism of the wear process that occurs clinically and to determine the physical test procedures and the data that will enable a correlation to be made between the physical/mechanical properties of the composite system and its durability.

Preliminary results with various stages of wear equipment modification have been promising but not definitive. Several steps have been taken to improve the precision of the data. Both the precision and the stability of the data generating process have been improved. Currently and for several months efforts will be concentrated on incorporating the new data acquisition equipment which replaces that of the Air Force previously used, a reinterfacing of the apparatus and a testing of its performance with several standard materials. Initially examination of commercial composite systems will involve the use of human enamel slider pins (the pin component of a pin on disc apparatus) but we intend to examine the feasibility of using substitute pin materials such as a hydroxyapatite ceramic which we have machined to appropriate size. Synthetic slider pins would appear to be a requirement if a standard testing procedure is to be developed.

Plans for an investigation of the durability-controlling micro-deformation mechanisms associated with the wear process have been made in detail. The rate of each contributing micro-deformation mechanism at various applied stresses and with different environments is to be determined. These micro-deformation mechanisms are assumed to include craze and shear band initiation and their growth in the matrix materials and the interfacial failure between the plastics matrix and the inorganic reinforcing particulate materials. Electro-hydraulic test equipment is being purchased that will allow for an investigation of the fatigue crack propagation mechanism in both matrix polymers and the interface of the dental composites under the mixed stress mode. The possibility of applying cumulative damage theory to the wear of dental restorative composite systems will also be explored.

Technical Activity

Accuracy of Fit and Castability

Cmdr. Richard Whitlock, DTC Edward Parry

While extensive efforts were made in this area in the two years preceeding (summarized in a manuscript in review by the Journal of Dental Research), we have examined one additional alloy of special concern to the U.S. Navy. We have also been determining the influence of casting into molds for which the investment material is being mixed with and without vacuum. Of particular interest is the possibility that the use of vacuum may produce smoother surfaces on the castings. The possible advantage of employing Kaowool, a refractory felt-like material, as the ring-liner in place of asbestos is being looked at more carefully. We have established that Kaowool is significantly more compressible than asbestos and is more uniform in its consistency allowing more predictable expansion characteristics.

While an experimental system for measuring the castability of dental alloys has evolved as a result of this project, modification is being sought to reduce the variability in the test results.

Porcelain to Metal Bonding

Cmdr. Richard Whitlock, DTC Edward Parry
H. Weber

A study of six commercially available dental bonding procelains has been undertaken. Precise dimensional changes resulting from the heating and cooling cycles are being observed with a differential dilatometer. Eight casting alloys are being examined similarly. Variables include the total number of firings and differing load conditions. Preliminary findings indicate that variations in the number of firing cycles and the amount of condensation of the green porcelain causes significant differences in dimensional characteristics on cooling of fused dental porcelain. Indications are that the resistance of the porcelain to flow under load increases with repeated firings and that ceramic materials from different manufacturers vary markedly in their dimensional response to thermal changes. The data collected to date suggest that varying degrees of residual stresses exist in different dental procelains when cooling rates follow those prescribed by the respective manufacturers. These types of data will serve as a basis for technique refinements aimed at improving the bond strength of procelain-fused-to-metal restorations.

Initial observations suggest that the characteristics of the wetting of base metal alloys by dental porcelains during fusion may

vary greatly with differences in alloy composition as well as with surface preparation techniques. Stereoscopic and cross-sectional photographs made through the scanning electron microscope will provide direct observation of this phenomenon. The information thus gathered will be extremely valuable in developing specific modifications of existing laboratory techniques. Suitable specimen design has been completed and the technique for photographing this surface activity is being refined. Dr. Weber, guest worker for a year from the University of Düsseldorf, is providing considerable input to this phase of the effort. Recommendations for modifying present surface preparation techniques will follow this phase of the investigation.

Technical Activity

Protein Adsorption, Surface Analysis and Surface-Protein Interaction Phenomena

R. E. Dehl, W. H. Grant, C. L. Allnutt

This research effort has provided physical science characterization support to the Biomaterials Program of the National Heart, Lung and Blood Institute of NIH. NBS competence in ellipsometry as applied to synthetic polymers led to the adaptation of this technique to the study of the interactions of blood proteins with solid surfaces.

When an implant device is placed into contact with blood, the initial event is the adsorption of proteins onto the surface. The nature of this adsorption, *i.e.*, the proteins involved, their absolute and relative amounts, the conformational changes of the proteins, the number and types of binding sites, the spatial distribution of the protein across the surface, potentially affect the later stages of the interaction of the formed elements with the implant. Since the initially deposited protein layer serves as the substrate for deposition of platelets and other blood elements which can lead to formation of a thrombus, it seems likely that the detailed characteristics of the protein layer play a major role in determining the ultimate success or failure of the implant.

Qualitative measurements on adsorbed proteins can serve as methods of surface characterization to aid in the selection and design of materials for implant use and as the basis for development of *in vitro* test methods for candidate implant materials.

A significant barrier to the development of *in vitro* test methods that correlate with *in vivo* evaluations is a lack of an assessment of surface homogeneity of candidate materials. The *in vivo* response is largely governed by the worst spots on the surface whereas *in vitro*

tests generally measure average surface properties.

We have previously demonstrated that the technique of ellipsometry is capable of detecting changes specifically to the surface energy of the substrate, the surface population of protein and the applied potential on the surface. These studies on model surfaces encouraged us to make ellipsometric measurements of protein adsorption on materials prepared by contractors of the Biomaterials Program and compare those results with forthcoming *in vivo* evaluation of the materials. These data should provide a better understanding of the factors governing the response of the blood to an implant.

We will continue investigating the response of candidate implant materials to important plasma proteins, using ellipsometry to determine the thickness and amount of adsorbed protein, and radiotracer labeled proteins to determine the amount of protein deposited, the distribution of protein on the surface, competitive adsorption from mixtures of proteins, and the penetration of proteins into hydrogel-coated implant materials. We anticipate initiating the use of secondary ion mass spectrometry (SIMS) to study the lateral distribution of proteins on surfaces, and their depth of penetration into the substrate.

Some of the elastomeric biomaterials selected for physical testing by the NHLBI Biomaterial Program for use in cardiac assist devices will undergo extensive flexing or cyclic deformation in a physiological environment for an extended time period. Therefore, it is important to investigate the adsorption, desorption and exchange of blood proteins on these materials before and after flexing. Thus, we propose to investigate the adsorption, desorption and exchange of blood proteins from plasma and whole blood on these elastomeric materials before and after flexing for the development of *in vitro* test methods for surface characterization of candidate cardiovascular implant materials.

Current trends are to use polymeric materials in more critical applications where long term performance in the service environment without deterioration of mechanical properties is of paramount importance. The reuse of polyethylene shipping containers for hazardous materials transportation raises questions about long term mechanical integrity, especially with ladings which may be even mild stress cracking agents. Elastomeric bladders are being designed for circulatory assistance devices where fatigue life in the physiological environment is a vital aspect. Test methods and standards are needed in order to ascertain the physical limits of polymeric materials in various use environments. Evaluation and control of materials parameters which affect long term performance should lead to more durable materials and, hence, reliable performance for the intended service life and environment.

The objectives of the task are to identify and analyze the principal failure mechanisms in polyethylene and biocompatible elastomers under mechanical stress in the use environment. An integral part of these objectives is to determine relationships between microstructure, mechanical properties and mechanisms at the molecular level which affect mechanical durability. To reach the objectives requires an interdisciplinary approach combining competences in mechanical properties measurements, fracture mechanics, continuum mechanics, chemistry and physics of molecular processes, spectroscopic techniques of infrared, Raman and nuclear magnetic resonance, x-ray scattering and electron and optical microscopy. The staff assigned to the projects listed below has the necessary expertise in these areas. Time resolved x-ray diffraction is a rapidly developing technique which shows promise for investigating relationships between microstructure and mechanical properties. Full utilization of this method would require staff additions.

Technical Activity

Mechanical Durability of Polyethylene Shipping Containers

J. M. Crissman, L. J. Zapas, G. B. McKenna, G. M. Martin, R. W. Penn and E. A. Kearsley

Plastics are finding wider use as shipping container materials due to their compatibility with many hazardous ladings and as a result of the energy savings in transportation afforded by lightweight container materials. Current trends include reuse of these containers in the transportation system. The Department of Transportation has regulatory responsibility for transportation of hazardous materials and has asked for assistance in developing test methods and data pertaining to the mechanical durability and reuse of plastic shipping

containers. The objectives of the project are to develop improved
test methods for stress-crack resistance, degree of crosslinking,
and service life prediction as well as to provide the DOT with a
test protocol for assessing the permeability of ladings in polyethy-
lenes of the sort used in container materials.

Time to failure experiments under uniaxial deformations for
polyethylene specimens of different molecular weight and molecular
weight distributions have been carried out as a function of tempera-
ture for environments which include air, stress cracking agents, and
swelling agents. Uniaxial creep data has been represented in terms
of isochrones which form a phase diagram including failure envelopes
for both necking and fracture. Phase diagrams were obtained for
several linear polyethylenes of similar weight average molecular
weight, but different number average molecular weight. Such repre-
sentations are extremely useful in determining physical and molecular
parameters which affect the amount of extension obtainable in uniaxial
creep. Based on the isochronal phase diagrams a study has been initi-
ated on the mechanical behavior of drawn polyethylene. Drawn fibers
of several types of polyethylene were obtained and the extensional
modulus and creep behavior examined as a function of draw ratio,
temperature and geometric constraints (clamped or free ends). Materi-
al instability which leads to necking in a specimen subjected to
uniaxial creep deformation under constant load can be described by
the BKZ theory with a proper definition of a time dependent strain
energy density function.

Data obtained in this laboratory on the logarithmic decrement
of free vibration in torsion superimposed on large uniaxial extensions
for polyethylene rods subjected to a constant load creep history
indicated the existence of a material instability. Application of
the BKZ theory to derive an analytic solution for such an experiment
is limited since numerical methods would be needed to find the inverse
of a complicated expression. Instead, the problem of a rod subjected
to a single step stress relaxation in extension with superimposed
sinusoidal deformations in torsion was solved for the storage and loss
moduli. If λ is the extension ratio, w is the angular frequency, and
t is the time after which the step was introduced, then we get

$$G'(\lambda, t; \omega) \over \omega = \left[\frac{\lambda^2 (G_{11} - G_{22})}{\lambda^2 - 1/\lambda} + G'(\omega) - G(t) \right]$$

and

$$G'(\lambda, t; \omega) = G'(\omega)$$

where $G'(\omega)$ and $G(t)$ are the storage modulus and the shear relaxation
moduli of the unstretched material. These results clarify certain
experimental results already in the literature.

The next phase of the project is concerned with biaxial deformation histories which are more realistic of expected service conditions experienced by large plastic containers. Data are obtained on polyethylene specimens in air and in presence of stress cracking agents using an inflated bubble testing apparatus. Calculations will be extended to the determination of instabilities which may occur for other types of strain histories including biaxial and fatigue types. Fatigue behavior leading to failure in poly(methyl methacrylate) has been evaluated within the framework of linear additivity of damage. Experimental results obtained in uniaxial tension indicated that linear additivity of damage does not describe the fatigue behavior of PMMA, and cannot be used as a tool to estimate the mechanical reliability of PMMA. Future work aimed at description of mechanical damage and fatigue in poly(methyl methacrylate) will focus on investigations of waveform effects and long time data. Since the simple linear additivity of damage hypothesis has shown to be invalid theoretical work will be aimed at developing a nonlinear damage law using the concept of a history dependence of the damage weighting function.

Characterization of Polymeric Materials Using Spectroscopic Methods

B. M. Fanconi, J. Mazur, D. L. VanderHart and J. F. Rabolt (NBS-NRC Postdoctoral Research Associate)

Polymeric materials exhibit a strong dependence of useful properties, such as mechanical strength and durability, on microstructure. Measurement techniques are needed which can detect those property sensitive structural features which, to date, are poorly characterized. Work in this project is centered on characterization of orientation and structure in semicrystalline polymers using Raman spectroscopy, normal coordinate analysis and carbon-13 nuclear magnetic resonance (C-13 NMR). The quantity and orientation of amorphous material, as well as the thickness, orientation and distribution of lamellar structures are important aspects of semicrystalline polymers which affect mechanical properties. The development of high tensile modulus polymer fibers, needed for reinforced composite materials to produce lightweight structures, requires knowledge of the degree of amorphous chain orientation and the ultimate tensile modulus. The latter quantity depends upon the polymer's structure and chemical bonding, and provides a limiting value against which processing methods for producing high modulus polymeric fibers can be evaluated. The ability to detect Raman bands whose frequencies are sensitive to lamellar crystal thicknesses has been demonstrated by observations on fluorinated polymers, polyethers and polyolefins. An added benefit of the technique is that the measurements yield the value of the Young's modulus for the crystalline material. The ultimate property value, thus determined, provides a goal against which new, evolving techniques for preparing high tensile modulus polymeric materials can be assessed. Ultimate modulus values have been shown to be as much as a factor of five higher than values determined by x-ray diffraction studies and have cast doubts on approximations inherent in the x-ray method.

Solid state C-13 NMR is uniquely suited for investigations of the quantity and orientation of one structural entity in presence of another. Since noncrystalline material has different relaxation times than crystalline material, it is possible to select out signals arising from just the noncrystalline material. In highly oriented, high tensile properties polyethylene produced by solid state extrusion, it has been found that the noncrystalline, or mobile fraction, is highly oriented, as is the crystalline component. Furthermore, the amount of noncrystalline material has been determined. The C-13 NMR facility has been modified so that experiments combining cross-polarization in conjunction with magic angle sample spinning could be performed. Sample spinning greatly reduces the linewidth of solid state NMR signals associated with chemical shift anisotropy and the cross-polarization technique reduces line broadening arising from dipolar

coupling. Resolutions approaching those obtained in liquids are possible by combining cross-polarization techniques with sample spinning.

Normal coordinate calculations have been carried out to estimate the dependence of vibrational Raman intensities on small changes in the chain geometry. A method for estimating the relationship between the scattering intensities of lamellar thickness dependent modes and the details of the molecular conformation has been verified. Thus, not only may the Raman measurements be used to determine the lamellar thicknesses, but also through the intensities may permit an estimate of the regularity of molecular conformation. One exciting possibility for this technique is to monitor the structural evolutions during thermal processing of polymeric materials.

A previous endeavor at the National Bureau of Standards has been the observation and analysis of Raman data arising from lattice vibrations whose frequencies are sensitive to the forces which hold the molecules in the regular crystalline array and which can be used to determine ultimate tensile properties in directions perpendicular to the change axis. These data provide a lower limit for bulk modulus values.

Future work will address the question of the possible effects of the structure of molecular chains near the lamellar surface on Raman frequencies and intensities. Such investigations are necessary in order to substantiate the ultimate tensile properties determined by Raman scattering.

Solid state NMR using sample spinning to obtain enhances resolution will be used to investigate molecular processes which lead to mechanical failure in elastomers. Crosslinking and molecular weight degradation are probably the principal molecular processes. An increase in chain mobility should accompany the breaking of chains. This increased mobility should show up as a change in relaxation time or linewidth in the rubbery states. The measurement of these parameters could, thus, become a measure of the extent of deterioration. The nature of the chemical degradation, *i.e.*, the chemical species produced by chain scission might be identified by swelling the polymer in a suitable solvent at elevated temperature and doing high resolution C-13 NMR.

Physical Testing of Polymers for Use in Circulatory Assist Devices

R. W. Penn, G. B. McKenna, J. M. Crissman, B. M. Fanconi, F. A. Khoury and G. W. Bullman

Left ventricular circulatory assist devices have been successfully employed in last-ditch efforts to give failed hearts time to recover following open heart surgery. The wider application of such devices to replace the heart for longer periods of time requires the development of blood compatible elastomeric materials capable of withstanding millions of cycles of mechanical stress in the physiological environment without adversely affecting bulk and physical properties. A Division project in cooperation with the National Heart, Lung, and Blood Institute is aimed at developing accelerated test methodology for prediction of service life of biocompatible materials under biaxial stress in physiological environment, and to apply the methodology to help identify suitable materials for use in circulatory assist devices which can function for two years or longer.

The extrapolation of short time measurements to predict long term performances must rely on a verified theoretical basis. The concept of a locus of material instability in stress, strain, and time coordinates together with linear additivity of damage are being applied. The instability can be detected in isochronal stress-strain plots for a series of tests with a given strain history. Both creep tests at various stress levels and stress relaxation tests at various strain levels are being exploited. Time to failure in such tests has been found to be a multiple of the time required to reach the instability point for polyethylene in uniaxial deformation. The mechanism leading to failure can be accelerated or other failure mechanisms activated by raising the temperature, by exposing the materials to various environments, and by increasing the stress or strain level of the test. Simulated use tests are carried out with cyclic biaxial stress conditions in a multiple station disc-inflation apparatus. Samples can be monitored for surface degradation by optical and electron microscopy and by attenuated total reflection infrared spectroscopy.

Research activities during the past year have centered on applying the test methodology to two different polymeric materials, characterization of a candidate biomaterial by optical microscopy and Fourier transform infrared (FTIR) spectroscopy, and preparation and distribution of an NBS standard butyl rubber to other laboratories involved in physical testing of biomaterials for circulatory assist devices for use as a standard for interlaboratory comparisons of test data.

Limited quantities of candidate materials available to us have permitted only preliminary measurements of constant strain rate and creep tests. The test methodology has been evaluated on a glassy polymer (polymethyl methacrylate) and a semicrystalline polymer (polyethylene). Deviations of fatigue data from predictions made from creep failure data were found to be in opposite directions for the two polymers. The NBS standard butyl rubber has mechanical properties similar to candidate biocompatible materials and will be used for test method development and verification. Surface studies of candidate polyurethane-polydimethyl siloxane biomaterial by optical microscopy and attenuated total reflection infrared spectroscopy has revealed significant differences between the two surfaces of the sheet material. The polydimethyl siloxane (PDMS) fraction is preferentially located near one surface and circular features observed near this surface by optical microscopy are likely to be regions of segregated PDMS on a much grosser scale than has been previously reported.

Preliminary design and construction of a biaxial fatigue test cell has been completed. Fatigue experiments on butyl rubber using this device have indicated that only minor modification will be necessary before initiation of fatigue testing on candidate biomaterials.

Steps have been taken to ensure adequate supplies of candidate biocompatible materials so that the next phase of the project will center on validation of the test methodology using these materials. Surface characterization will be carried out for quality control and for monitoring surface degradation during for time testing. A multiposition test station for biaxial fatigue experiments is being assembled. This device will be used to investigate environmental effects on mechanical durability.

Nonlinear Viscoelastic Behavior of Materials

G. B. McKenna and L. J. Zapas

Project objectives are to study the nonlinear viscoelastic behavior of materials and the description of this behavior using constitutive theory (BKZ elastic fluid) and to test the prediction that in a two-step stress relaxation experiment in torsion or shear, if the strain of the second step is one-half that of the first step, then the second step normal stress response is independent of the duration of the first step and equivalent to the single-step normal stress response at the strain level of the second step.

The nonlinear viscoelastic behavior of poly(methyl methacrylate) in torsion was characterized and it was found that the modified form of the BKZ theory which was used could describe the shear stress response in two-step histories for both unconditioned and mechanically conditioned poly(methyl methacrylate). However, the normal stress response was adequately described only for the mechanically conditioned material. Experiments were carried out using torsion deformations of poly(methyl methacrylate) and polyethylene t determine whether or not the prediction described above is true. Polyethylene data has not been completely analyzed, although initial results are encouraging.

Results from poly(methyl methacrylate) show that, within experimental error, the normal stress response in the two-step history for $\delta_2 = \frac{1}{2}\delta_1$ is the same as that for the single-step stress relaxation response at $\delta = \delta_2$. In addition, the response is independent of the time, t_1, (duration) of the first step over a range of $t_1 = 3.28s$ to $t_1 = 1678s$.

During the coming year, the data analysis on polyethylene will be completed and the strain potential derivatives, $\partial W/\partial I_1$ and $\partial W/\partial I_2$, for poly(methyl methacrylate) and polyethylene tubes will be determined. Preliminary work indicates that these primitive functions can be determined using the scaling law developed by Penn and Kearsley. The time dependent behavior observed for $\partial W/\partial I_1$ and $\partial W/\partial I_2$ will bear directly on the extension of the concept of a relaxation spectrum from linear viscoelasticity to nonlinear behavior.

Durability of Paper

E. Graminski, E. E. Toth and J. C. Smith

Paper is a relatively inexpensive, disposable material which doesn't require a lifetime much greater than a few months or years. However, since paper is used so prevalently for records it is essential that paper used for records will last anywhere from 100 to a 1000 years depending on the importance of the document. In addition to chemical stability, paper may be required to have good physical durability when used, for example, in currency. The cost of making documents, representing material value, is high and a long lifetime is required of the paper. Solutions to these problems necessitate considerable fundamental knowledge of the material. Since the quantity of paper, requiring high permanence and/or durability, is minuscule relative to the total amount of paper consumed, very little research on these properties has been conducted. To make matters worse, most of the research has been empirical rather than fundamental so that the data on permanence in the literature is questionable.

A somewhat unrelated problem deals with the disposability of paper. The major portion of municipal trash by weight consists of paper, and since paper is a very low density material the percentage of the volume represented by paper is even greater. These factors have resulted in wholesale efforts to recycle more paper in an effort to reduce the amount of solid municipal waste. Despite the advantages of increasing the rate of paper recycling, very little paper gets reused in applications replacing virgin paper. The antagonism towards paper recycling stems from a lack of real-time measurement techniques suitable for characterizing pulps made from waste paper. These measurement techniques are essential to increased paper recycling.

Results of the most recent investigation on the stability of paper indicate that the degradation rate of paper is directly related to the moisture content of paper. The effect of water on the degradation rate is very great at 80 ° and 90 °C signifying the necessity for precise control of temperature and humidity at these temperatures for reliable degradation results. It also indicates that the effect of moisture and temperature on the degradation of paper must be determined in any accelerated aging test since not all of the water, bound to cellulose, is "active" in the degradation process and the amount of "inactive" water may be different for each paper. No further work is contemplated for this project.

a measurement technique which is automatic and rapid. During the past year algorithms were constructed to make automatic measurements of fiber length distribution and curl. Also the flexibility of using a short-span tensile test for estimating the strength quality of pulp fibers was evaluated. The short-span tensile test appears promising for measuring fiber strength quality. No further work is being planned for the next fiscal year.

Statistical Mechanics of Polymer Systems

E. A. DiMarzio

The methods of statistical mechanics are applied to the development of a complete equilibrium description of molecular systems that form glasses and to the behavior of polymer molecules near surfaces. Polymer glasses are characterized by time scales that approach the time scales of experiments on glasses. On this basis it has been erroneously concluded that equilibrium properties are not relevant to glasses. However, since molecules which form glasses have calculable equilibrium properties and since all theories of time-dependent phenomena require prior knowledge of equilibrium statistical mechanics as a necessary point of departure it is essential that equilibrium properties be determined.

The physics of polymer molecules near surfaces are germane to a number of problems in polymer science and technology ranging from adhesion in a composite to wear of polymer surfaces. The pivotal problem common to all areas of application is calculation of the packing statistics of flexible bulk polymers near surfaces. Flexible isolated polymers near a surface and rigid bulk polymers near a surface are solved problems, but the problem of a flexible bulk polymer (bulk refers to the fact that interactions between different molecules must be taken into account) near a surface remains to be considered. Work is in progress on four aspects of this problem: 1) bulk polymer between parallel plates, 2) polymer in a density gradient of oriented bonds, 3) polymer in a cone, and 4) aspects of the amorphous-crystalline complex.

Present work on glasses includes: 1) an examination of experimental data to determine whether there are any unique relationships among the experimental thermodynamical quantities, 2) the addition of vibrational terms to the Gibbs-DiMarzio theory of glasses, and 3) calculation of time dependence of order parameters.

Theoretical Verification of Symmetry Tricritical Points in Binary Glass Mixtures of Chain Molecules

F. Dowell (NBS-NRC Postdoctoral Research Associate)

Tricritical points are of interest in the theory of phase transitions and critical phenomena. They are also of practical interest since they are concerned with phase separation in the region of the glass transition. The objectives of the project are to establish the existence of these points both from model calculations and experiments.

Lattice models are used in computer simulations to search for these points. Although their existence has not been conclusively established, conditions close to those required for these points have been found. The main difficulty arises in refining lattice models so that they are sufficiently sensitive to exhibit the behavior hypothesized. Even so, different situations involving phase separation near the glass transition have been observed.

From the theoretical predictions, experiments are being planned to locate tricritical points.

Permeation Measurements for Hazardous Materials Transportation

John D. Barnes, Gordon M. Martin, Frank L. McCrackin

The Office of Hazardous Materials Operations of the Department of Transportation has asked the Polymer Science and Standards Division for technical assistance in finding criteria and test methods for detecting combinations of ladings and plastic shipping containers which are mutually incompatible. This need arises from the introduction of new plastic products, based upon improved technology, into the transportation network. These containers are being considered for use in shipping certain hydrocarbons which can, at elevated temperatures, act as solvents for polyethylene. We have previously identified high density polyethylene resins as the most important materials to be considered in this application. We have also identified the permeability of a given lading through a given polyethylene resin at the most important single index of incompatibility.

Present techniques for screening out unsuitable combinations of ladings and containers are mostly based upon qualitative assessments of the performance of full-size shipping containers filled with the lading of interest under long-term storage at room temperature. We have been seeking a cheaper and quicker test as a candidate for inclusion in DOT's regulations governing hazardous materials shipments. We are also seeking to standardize measurement practices so that the results of testing can be applied to a broad range of cases.

During FY 77 we undertook a series of laboratory experiments to evaluate a simple method (ASTM D2684) for measuring the permeability of polyethylene with respect to various ladings. Polyethylene resins of two different densities were used. The ladings were members of the normal alkane series ranging from C_7H_{16} to $C_{18}H_{38}$. Measurements were made at three temperatures. The experimental procedure consisted of periodically measuring the mass of polyethylene bottles which had been filled with the permeant in question and placed in an oven at the desired temperature. The quantities which were extracted from the data were the steady-state rate of mass loss and the permeation time-lag. These two quantities were subjected to statistical analysis and the result was an empirical correlation which showed that the effect of chemical structure could be partly separated from the influence of measurement temperature and the state of the polymer (as characterized, for example, by the polymer density.)

The length of normal alkane chains provides a natural scale for ranking the permeability of chemical species in polymers. In this sense any chemical species can be assigned an "effective carbon atom number". Our experiments demonstrated that the effective carbon atom number of the n-alkanes was independent of temperature and the state of the polymer. This result supports the concept of the

"permachor" as developed by workers at the Plax Corporation in the late 1950's. These results provide a measure of confidence that the results of measurements using a standard polymer can be transferred to the products of industrial processes.

Further work needs to be done to ensure that effective carbon atom numbers can be assigned to permeants other than n-alkanes in a meaningful way and that the results are applicable to a sufficiently broad range of polyethylene resins.

Migration and the Durability of Plastics in Use

All plastic items found in commerce have low molecular weight substances incorporated in them, either as a result of their method of manufacture or from the purposeful incorporation of additives to produce or maintain desirable properties. In use, these substances inevitably diffuse through the polymer to some extent and may eventually migrate out of the polymer.

The consequences of migration are twofold. First, if the migrating substance is a stabilizing or property enhancing additive, the plastic is left with poorer properties or increased vulnurability to degradation and failure. This is a major failure mode of plastics and programs concerned with polymer durability must explicitly address the possibilities of additive migration. Second, the migrating substance becomes a contaminant of the general environment or, in the case of plastic packaging materials, a contaminant of the material being contained and so questions are raised about the toxicological consequences of such migration. Contamination of food from food packaging materials is regulated by the federal government through the Food and Drug Administration and the control of migrating substances presents an enormous challenge to the scientific basis of regulations.

The number of commercially usable polymer-additive combinations is too large to be considered efficiently on a case by case basis, either for selection of materials for optimum durability or for regulation of food and environmental contamination. General material models capable of predicting migration under a variety of service conditions are needed to organize polymer-additive combinations into classes for consideration. The development of these material models is the overall objective of work done in this task.

Two major technical activities contribute to this goal; the development of general thermodynamics theories of polymer solutions and the development of data and methods for the measurement of migration in polymers.

Technical Activity

A common element of the following subtasks is the application of the lattice fluid (LF) theory of solutions. A brief summary of this theory is given below.

A pure fluid is represented by a lattice occupied by N r-mers (each mer occupies one lattice site) with N_0 vacant sites. The configurational partition function is evaluated assuming random mixing of r-mers and vacant sites. To within an additive constant,

the reduced chemical potential, $\bar{\mu}^0$, for a pure fluid is given by

$$\bar{\mu}^0 = \mu^0/(Nr\varepsilon^*) = -\bar{\rho}^2 + \bar{P} + \bar{T} \left[(1-\bar{\rho})\, \ln(1-\bar{\rho}) + \bar{\rho}/r\, \ln\bar{\rho}\right]/\bar{\rho} \quad (1)$$

where $\bar{T}$, $\bar{P}$, and $\bar{\rho}$ are the reduced temperature, pressure, and density defined as

$$\bar{T} = T/T^* \; ; \; T^* \equiv \varepsilon^*/k \qquad (2a)$$

$$\bar{P} = P/P^* \; ; \; P^* \equiv \varepsilon^*/v^* \qquad (2b)$$

$$\bar{\rho} = \rho/\rho^* \; ; \; \rho^* = M/rv^* \qquad (2c)$$

ε^* is the total interaction energy per mer

v^* is the close-packed mer volume

M is the molecular weight

T, P, and ρ are the temperature, pressure, and mass density.

At equilibrium the chemical potential is at a minimum and satisfies the following equation of state:

$$\bar{\rho}^2 + \bar{P} + \bar{T}\left[\ln(1-\bar{\rho}) + (1-1/r)\bar{\rho}\right] = 0 \qquad (3)$$

The equation of state defines the value of $\bar{\rho}$ which minimizes the free energy at a given $\bar{T}$ and $\bar{P}$. Three parameters, either ε^*, v, and r or T^*, P^*, and ρ^*, suffice to characterize a fluid. These parameters can readily be calculated using PVT data and have been tabulated for a large number of low molecular weight fluids as well as a number of common polymers.

For a binary mixture, the reduced chemical potential of component 1, $\bar{\mu}$, is given by

$$\bar{\mu}_1 \equiv \mu_1/(Nr_1\varepsilon_1^*)$$

$$\bar{\mu}_1 = \bar{T}_1[\ln\phi_1 + (1-r_1/r_2)\phi_2] + (r_1\Delta P^*/P_1^*)\phi_2^2 + \qquad (4)$$
$$r_1\left\{-\bar{\rho}^2 + \bar{P}_1 + \bar{T}_1[(1-\bar{\rho})\ln(1-\bar{\rho}) + \bar{\rho}/r_1\ln\bar{\rho}]\right\}/\bar{\rho}$$

where $\bar{\rho}$ is the reduced density of the mixture of composition ϕ_1:

$$\phi_1 = 1-\phi_2 = \frac{m_1/\rho_1{}^*}{m_1/\rho_1{}^* + m_2/\rho_2{}^*} \tag{5}$$

and m_1 and m_2 are mass functions. The binary interaction parameter ΔP^* is the only unknown parameter for a binary mixture. It represents the net change in cohesive energy density that occurs upon mixing at the absolute zero of temperature and determines the sign of the heat of mixing at absolute zero.

Migration of Additives in Polymers

I. C. Sanchez

A polymer's usefulness is often determined by the rate at which a minor chemical constituent is released by the polymer. Obvious examples are the desorption of antioxidants and plasticizers. To quantitatively describe this phenomenon requires a knowledge of the diffusants' transport and thermodynamic properties within the polymer and in the environmental fluid phase. To date, most of our effort has been directed at the thermodynamic or equilibrium aspect of this problem.

When the volume of the environmental fluid is finite, diffusion of a minor chemical species will proceed until equilibrium is attained. At equilibrium the diffusing species will partition itself between the polymer and environmental fluid phases defined by a partition coefficient K. The estimation of K is an important consideration in drug release from polymeric delivery devices and in applications of polymers as food packaging materials.

We consider the specific system of a non-ionic diffusant in an amorphous or semi-crystalline polymer in contact with a liquid at temperatures above glass temperature, T_g. The liquid may be a good or poor solvent for the polymer. For this type of system a theoretical relation can be obtained for K by applying the LF theory.

In the absence of solvent absorption, we have shown that the partition coefficient is given by

$K_o \equiv$ solvent diffusant cone/polymer diffusant cone

$$\ell n K_o = r_d \left(1/r_s + \chi_s^\infty - \chi_p^\infty\right) \tag{6}$$

where r_d and r_p is the number of sites occupied by diffusant and solvent molecules, respectively, (defined by Eq. 2c) and χ_s^∞ and χ_p^∞ are the infinite dilution values of diffusant-solvent and diffusant-polymer interaction parameters. (It is assumed that the diffusant is present in low concentrations). A zero subscript has been attached to K to remind us that Eq. (6) is only valid when solvent is not absorbed by the polymer.

The interaction parameters χ_p^∞ and χ_s^∞ can be determined experimentally or the LF theory can be used to calculate them:

$$\chi_s^\infty \equiv \bar{\mu}_s \,(\phi_s = 1) - \bar{\mu}_s^{\,o}$$

$$\chi_s^\infty = \bar{\rho}_s \Delta P_s^* / P_d^* \bar{T}_d + (\bar{\rho}_d - \bar{\rho}_s)/T_d + 1/r_d \ell n (\bar{\rho}_s/\bar{\rho}_d) + \tag{7}$$

$$(1-\bar{\rho}_s) \ell n (1-\bar{\rho}_s)/\bar{\rho}_s - (1-\bar{\rho}_d) \ell n (1-\bar{\rho}_d)/\bar{\rho}_d$$

where the subscripts d, s, and p refer to diffusant, solvent, and polymer, respectively. A similar expression holds for χ_p^∞ (replace s by p).

When solvent is absorbed by the polymer, we have shown that the partition coefficient is given by

$$\ell n K = \ell n K_o - \phi_s \left\{ \ell n K_o - \frac{r_d}{r_s} \left[\frac{\ell n \phi_s}{1-\phi_s} + 1 \right] \right\} \tag{8}$$

where ϕ_s is the concentration of solvent absorbed at equilibrium. For a semi-crystalline polymer ϕ_s refers to the concentration within the amorphous regions since it is assumed that solvent is excluded from crystalline domains. Notice that $K \to K_0$ as $\phi_s \to 0$ and $K \to 1$ as $\phi_s \to 1$ as it should.

Inspection of Eq. (8) reveals that if $K_0 > 1$, i.e., if partitioning favors the solvent phase, absorption of solvent lowers the partition coefficient ($K < K_0$). This effect can be best understood by imagining the partitioning to occur in two steps. In the first step the diffusant partitions in the absence of solvent absorption preferentially toward the solvent phase ($K_0 > 1$). In the second step,

solvent containing some of the diffusant is abosrbed by the polymer. Thus, the diffusant is abosrbed by the polymer. Thus, the diffusant is reabsorbed literally on the "coattails" of the solvent.

When $K_0 < 1$, Eq. (8) suggests that it is possible for solvent absorption to increase the partition coefficient ($K > K_0$). The exact conditions for this occurence are

$$X_s^\infty > X_p^\infty + \frac{\ell n(1/\phi_s)}{r_s(1-\phi_s)} \tag{9}$$

Under these conditions we have a reverse coattail effect. It can be understood as follows: A small K_0 implies a poor solvent-diffusant interaction (large positive X_s^∞) and the diffusant prefers to remain in the polymer phase. When solvent is absorbed, the diffusant now "sees" a thermodynamic environment in the polymer phase that is similar to the one in the solvent phase, neither of which it likes. Since the disparity in thermodynamic environments is reduced by solvent absorption, the diffusant tends to redistribute itself more evenly between the two phases.

Phase Separation

I. C. Sanchez

A general result of the LF theory is that differences in equation of state properties of the pure components makes a thermodynamically unfavorable entropic contribution to the chemical potential. This is most apparent in the stability condition (the spinodal). For a binary mixture at a given temperature and pressure, a necessary and sufficient condition for miscibility over the entire composition range is for $d \mu_1/d \phi_1$ to be positive over the entire range. From Eq. (4) this translates to

$$\frac{1}{2}\left[\frac{1}{r_1\phi_1} + \frac{1}{r_2\phi_2}\right] - \tilde{\rho}\left[\frac{\Delta P^*}{P^*\tilde{T}} + \frac{1}{2}\Psi^2\tilde{T}P^*\beta\right] > 0 \tag{10}$$

$$\underbrace{\qquad\qquad\qquad}_{\substack{\text{combinatorial}\\\text{entropy}\\\text{combination}}} \underbrace{\qquad}_{\substack{\text{energetic}\\\text{combination}}} \underbrace{\qquad}_{\substack{\text{entropic contribution}\\\text{from equation of state}}}$$

where $\tilde{T}$, P^* and β are the reduced temperature, characteristic pressure, and isothermal compressibility of the mixture of composition ϕ_1; Ψ is a function of composition and temperature and can be expressed in terms of differences of the pure component parameters.

The salient point is that the entropic equation of state term is proportional to the compressibility of the mixture and, since it is always positive, makes an unfavorable contribution to the spinodal; i.e., its presence never favors miscibility. Thus, differences in pure component parameters, especially T^* values, tend to destabilize a solution and make it more susceptible to phase separation. This unfavorable entropic term, which is small and relatively unimportant at low temperatures, becomes large and dominant as the liquid-gas critical temperature T_c is approached. In both low molecular weight and polymer solutions this term is similar in magnitude, but the favorable contribution that the combinatorial entropy makes toward stability is much smaller for polymer solutions. This small combinatorial entropy term makes a polymer solution more susceptible to phase separation (than a similar low molecular weight solution) at both low and high temperatures. Therefore, we reach the general conclusion that in non-polar polymer solutions limited miscibility at low and high temperature is a manifestation of a polymer solution's small combinatorial entropy.

Heats of mixing at infinite dilution $\Delta H_m(\infty)$ have been used to determine the interaction energy parameter ΔP^* between polyisobutylene (PIB) and seven hydrocarbon solvents. As might be expected for these non-polar solutions, the calculated ΔP^*'s are all positive. Thus, at absolute zero the heats of mixing would all be positive (endothermic). However, of the seven solutions, only one (PIB/benzene) has a positive heat of mixing at 25°C. In terms of the LF theory, negative heats are caused by the tendency of the solvent to contract when a small amount of polymer is added. The magnitude of the contraction is proportional to the isothermal compressibility of the solvent. It is an energetically favorable process because it results in more intermolecular interactions of lower potential energy, but it is entropically unfavorable because of the densification.

Although $\Delta Hm(\infty)$ is large and positive at room temperature for PIB/benzene, it decreases with increasing temperature and becomes exothermic near 435K. LF theory semi-quantitatively accounts for this behavior as shown in Figure 1 (solid circles are experimental points and the line is calculated).

Chemical potentials have been calculated in both dilute and concentrated ranges and compared with available experimental data on PIB solutions of n-pentene, n-octane, cyclohexane, and benzene. The essential validity of the theory is manifested in the calculated values of the reduced residual entropy at infinite dilution ($\chi_{s;1}$). In classical (Flory-Huggins) theory $\chi_{s;1}=0$, yet $\chi_{s;1}$ dominates the chemical potential in these dilute PIB solutions. Calculated $\chi_{s;1}$ values are in good agreement with those observed except for benzene.
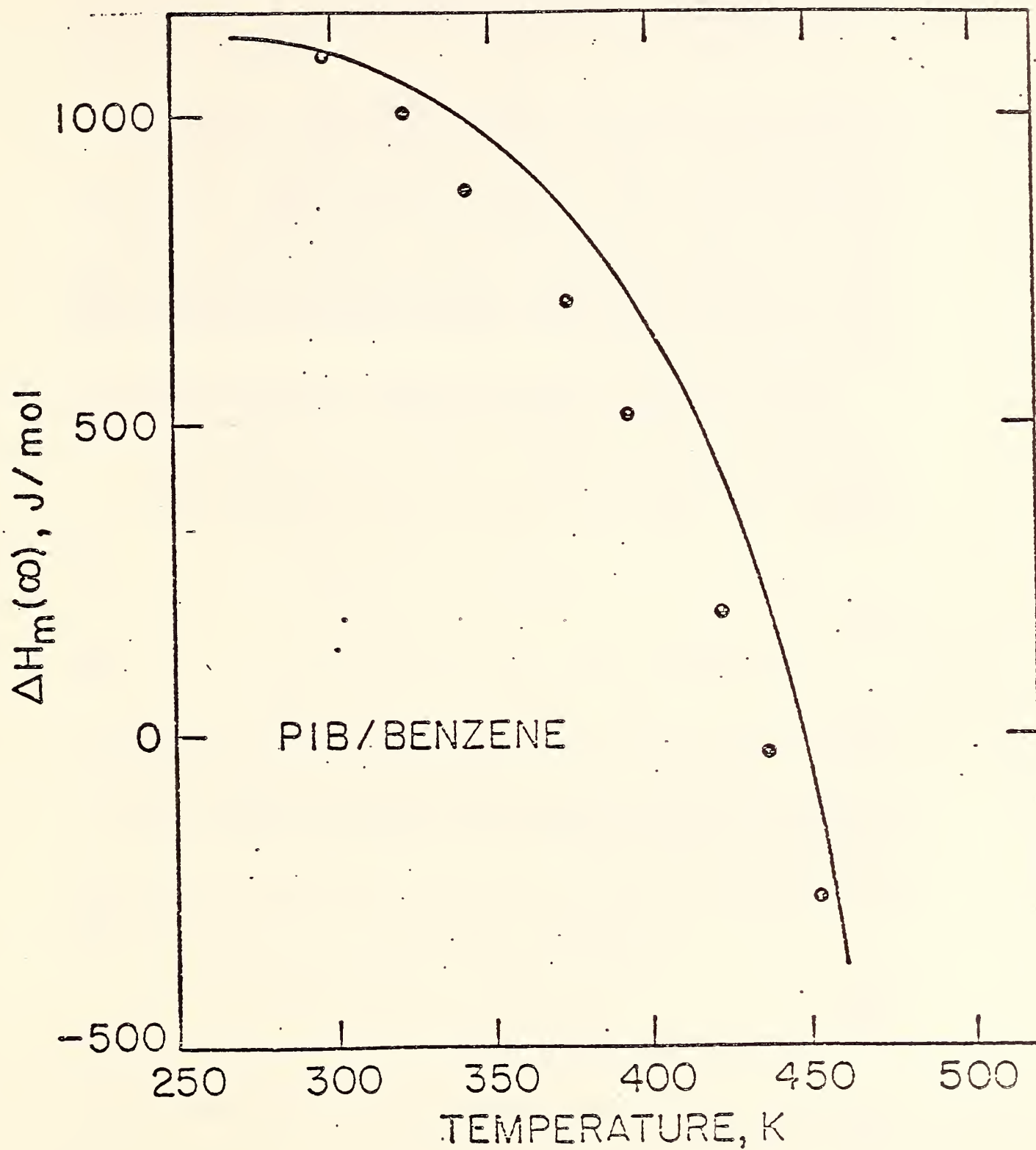
Figure 1

Molecular Theory of Surface Tension

I. C. Sanchez and C. I. Poser

Using the lattice fluid model in conjunction with the Cahn-Hilliard (CH) theory 5,6 of inhomogeneous systems, a method has been developed for calculating the surface tension of both low and high molecular weight liquids with high accuracy. Motivation for this work arises from a number of sources. First, there is the desire to develop a unified approach applicable to both low molecular weight liquids and polymer melts. Such an approach should give us a better understanding of the relationship between molecular properties and surface tension. Second, this surface tension theory can be extended to yield a more general interfacial tension formulation for polymer mixtures.

CH theory provides a means of relating a statistical mechanical model of a fluid to surface properties. In passing from liquid to vapor through the interfacial region, the fluid density, ρ, passes from a high to low value. According to CH theory, the Helmholtz free energy density, a, of a fluid containing a density gradient can be expressed in terms of ρ and its derivatives:

$$a(\rho, \nabla\rho, \nabla^2\rho, \ldots) = a_0(\rho) + \kappa_1 \nabla^2\rho + \kappa_2 (\nabla\rho)^2 + \ldots \tag{11}$$

where

$$\kappa_1 = \partial a/\partial\nabla^2\rho \bigg|_0 \quad \text{and;} \quad \kappa_2 = \frac{1}{2}\partial^2 a/(\partial|\nabla\rho|)^2 \bigg|_0 \tag{12}$$

and $a_0(\rho)$ is the free energy density of a uniform fluid of density ρ.

The subscripts 0 in eq. 2 indicate that the derivatives are to be evaluated in the limit of $\nabla\rho$ and $\nabla^2\rho$ going to zero. If the density variation is sufficiently slow, the total free energy of the fluid, A, is given by

$$A = \int_V [a_0(\rho) + \kappa(\nabla\rho)^2]dV \tag{13}$$

where

$$\kappa = -d\kappa_1/d\rho + \kappa_2 \tag{14}$$

Using these relations, the surface tension, σ, for a planar interface can be written as

$$\sigma = \int_{-\infty}^{\infty} [\Delta a + \kappa(d\rho/dx)^2]dx \tag{15}$$

where x is the direction perpendicular to the interface and $\Delta a = a_o e^{-a}$ is the difference between the Helmholtz free energy density of a homogeneous fluid of density ρ and a two-phase equilibrium mixture of the same density. Minimization of eq. 5 with respect to the density gradient yields

$$\sigma = 2 \int_{\rho_g}^{\rho_\ell} [\kappa \Delta a]^{1/2} d\rho \qquad (16)$$

$$\left(\frac{d\rho}{dx}\right)^2 = \Delta a / \kappa \qquad (17)$$

where ρ_g and ρ_ℓ are the homogeneous gas and liquid densities. LF theory can be used to evaluate both Δa and κ.

Using LF theory, Eq. (16) can be conveniently rewritten in dimensionless form (all tilde quantities are dimensionless):

$$\tilde{\sigma} = 2 \int_{\tilde{\rho}_g}^{\tilde{\rho}_\ell} (\tilde{\kappa} \Delta \tilde{a})^{1/2} \, d \tilde{\rho} \qquad (18)$$

where

$$\tilde{\sigma} = \sigma/\sigma^* \; ; \; \sigma^* = \epsilon^*/v^{*2/3} \qquad (19)$$

$$\tilde{\kappa} = \kappa/\kappa^* \; ; \; \kappa^* = v^{*2/3} \qquad (20)$$

$$\Delta \tilde{a} = -\tilde{\rho}^2 + \tilde{P}_o + \tilde{T} [(1-\tilde{\rho})\ln(1-\tilde{\rho}) + \frac{\tilde{\rho}}{r} \ln \tilde{\rho}] - \tilde{\rho} \, \tilde{\mu}^o \qquad (21)$$

where $\tilde{P}_o$ is the equilibrium vapor pressure and $\tilde{\mu}^o$ is the equilibrium chemical potential

$$\tilde{\mu}^o = \tilde{\mu}^o (\tilde{T}_1 \tilde{P}_o, \tilde{\rho}_\ell) = \tilde{\mu}^o (\tilde{T}, \tilde{P}_o, \tilde{\rho}_g) \qquad (22)$$

given by Eq. (1).

To determine $\bar{\kappa}$ for the LF, we adopt the standard assumption that the entropy of the inhomogeneous system depends only on the local density and is independent of the density gradient. In this case, the gradient only affects the potential energy. We assume a Sutherland type potential (hard core plus attractive tail) for the interaction between mers as a distance R, i.e.,

$$\varepsilon(R) = \begin{cases} \infty & R/v^{*1/3} < 1 \\ -\varepsilon_o (v^{*1/3}/R)^n & R/v^{*1/3} > 1 \end{cases} \tag{23}$$

For this potential, the characteristic LF interaction energy, ε^*, is given by

$$\varepsilon^* = 2\pi\varepsilon_o/(n-3) \tag{24}$$

and

$$\bar{\kappa} = \frac{1}{6} \frac{n-3}{n-5} \tag{25}$$

For the usual value of $n = 6$, $\bar{\kappa} = 1/2$.

Figure 2 illustrates calculated values of $\bar{\sigma}$ as a function of reduced temperature, $\bar{T}$, for various values of r. These curves qualitatively predict that for a homologous series of liquids, the surface tension increases and the surface entropy, $-d\sigma/dT$, decreases with increasing r or molecular weight. Both of these predictions are in qualitative accord with experiment.

In principle, calculation of the surface tension involves no adjustable parameters, since the three LF parameters are determined from PVT data. In practice, however, we find that the calculated values of σ are usually too low for the ab initio value of $\bar{\kappa} = 1/2$ which is based on an attractive potential of the inverse sixth power type. If $\bar{\kappa}$ is treated as an adjustable parameter, we find that a constant value of $\bar{\kappa} = 0.62$ can be used for a variety of non-polar and slightly polar liquids over a wide temperature range, $0.4 < T/T_c < 0.75$, with a maximum error of less than 5% (T_c is the gas-liquid critical temperature). This value of $\bar{\kappa}$ corresponds to n = 5.74 in Eq. (25).
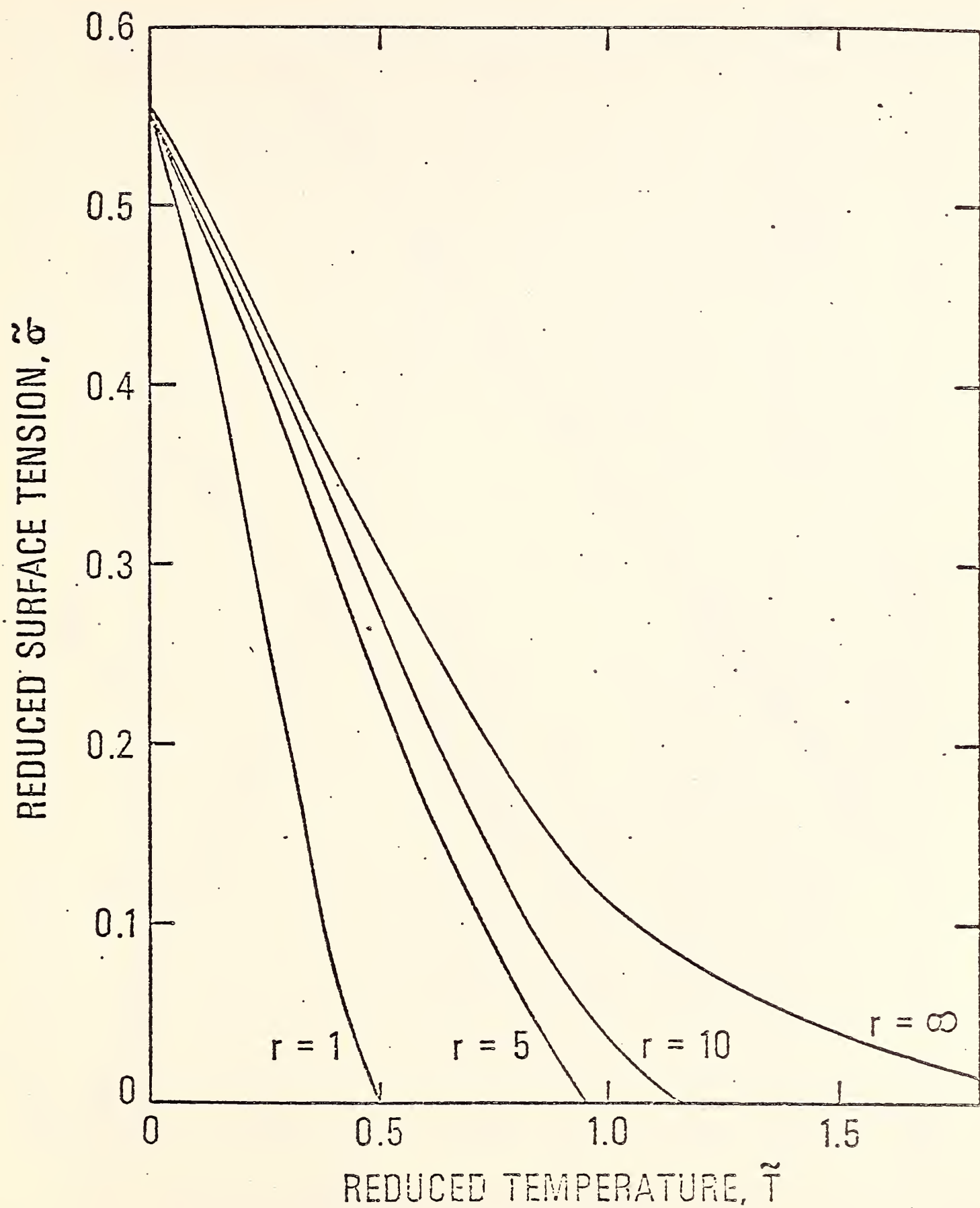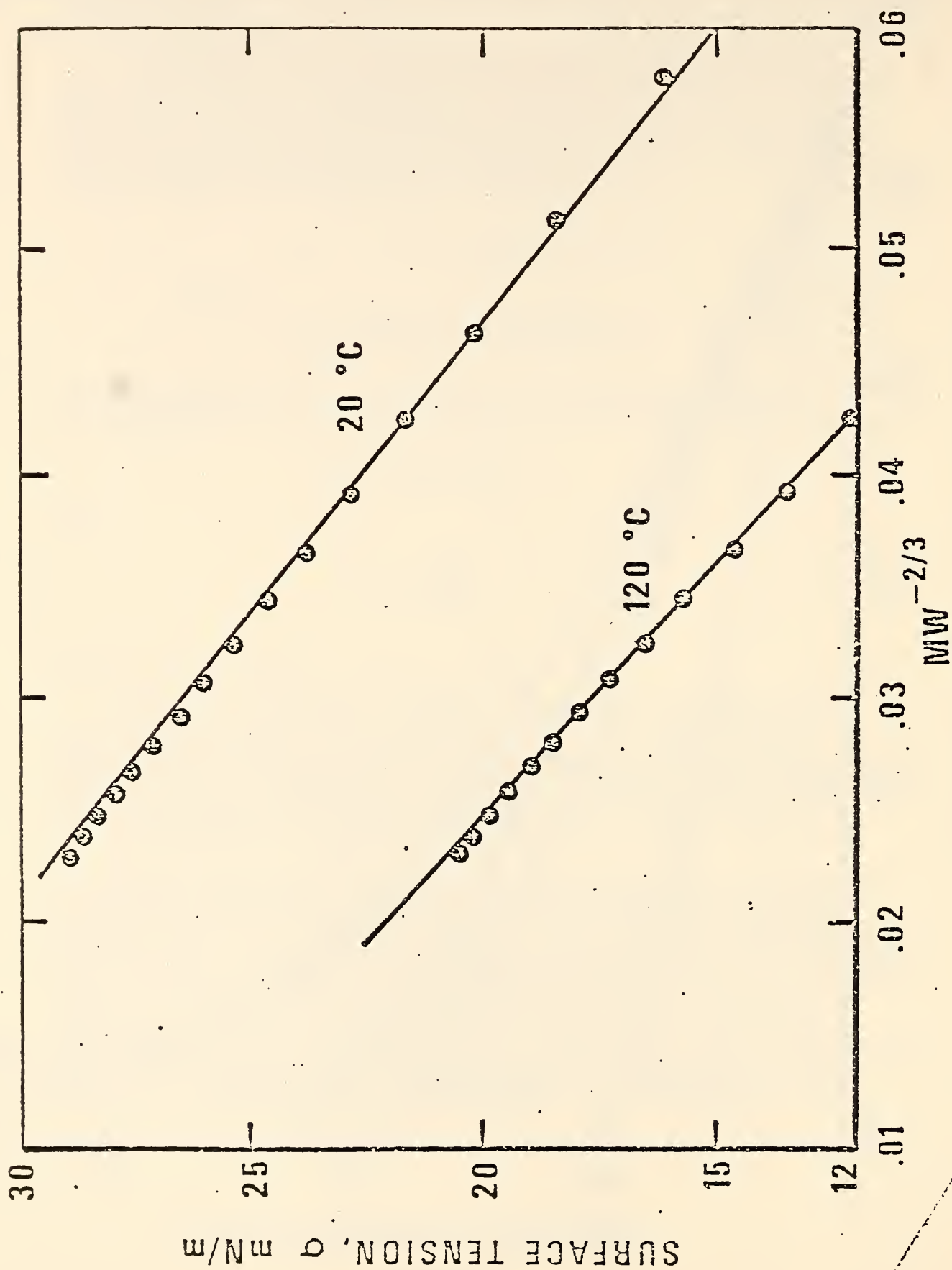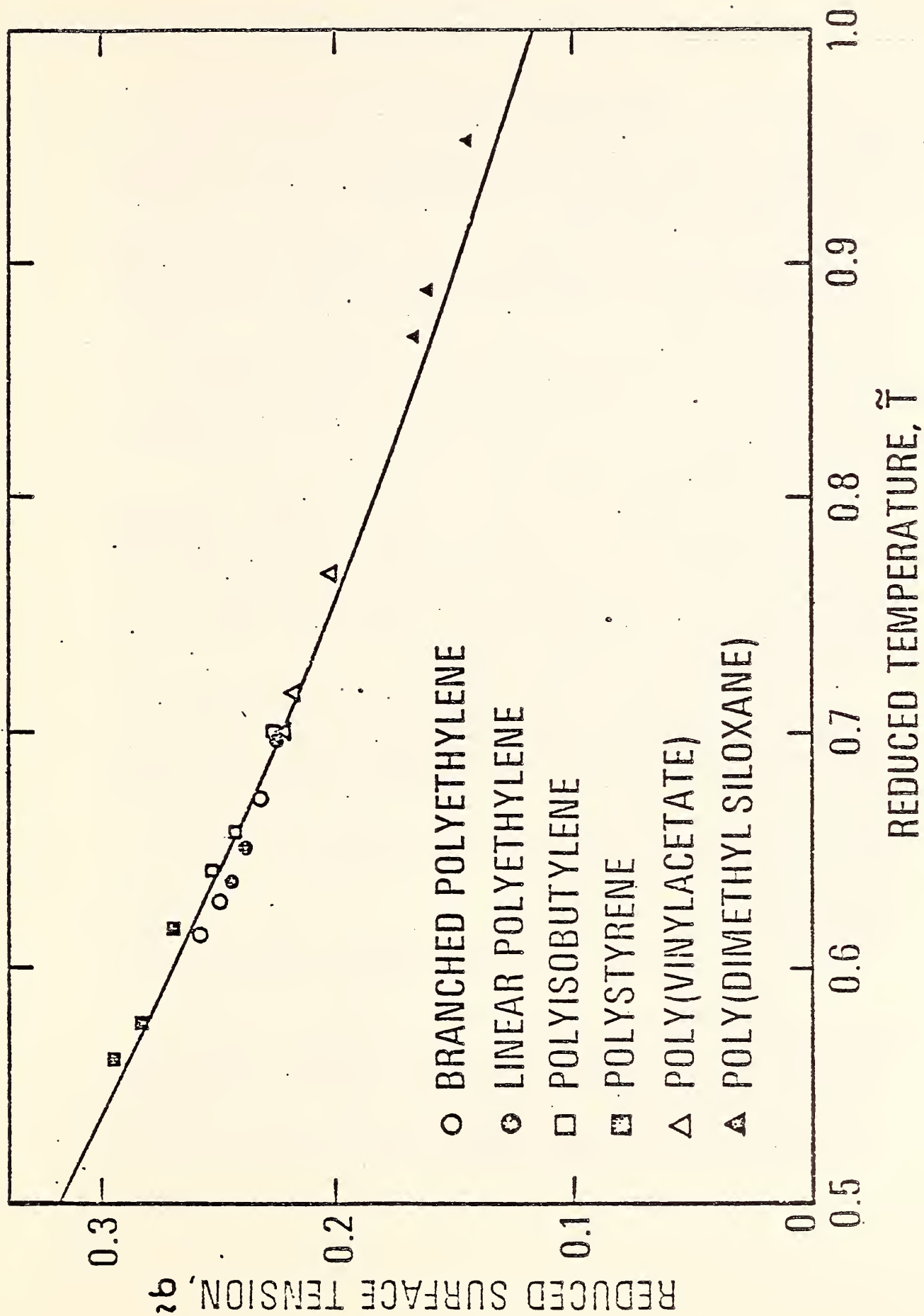
Figure 2
4-149

igure 3

REDUCED TEMPERATURE, $\tilde{T}$

Figure 4

○ BRANCHED POLYETHYLENE
⊕ LINEAR POLYETHYLENE
□ POLYISOBUTYLENE
▣ POLYSTYRENE
△ POLY(VINYLACETATE)
▲ POLY(DIMETHYL SILOXANE)

REDUCED SURFACE TENSION, $\tilde{\gamma}$

Empirically, it has been discovered that surface tension is molecular weight (M) dependent and varies as $M^{-2/3}$. This type of behavior is illustrated in Figure 3 for the n-alkanes at two temperatures. The solid line is a theoretical line based on $\kappa = 0.61$ (n = 5.75) and the solid circles are experimental points. As can be seen, the fit is excellent.

As r increases, $\bar{\sigma}$ approaches a limiting value, $\bar{\sigma}_\infty$, which implies a corresponding states principle for polymer melts of sufficiently high molecular weight. In Figure 4 σ_∞ is plotted as a function of T and compared with experimental data for six polymers. A value of $\bar{\kappa} = 0.55$ (n=5.85) yields a good fit to the data. Absolute values of σ range from a high of 32.1 dyne/cm for polystyrene to a low of 12.1 dyne/cm for poly(dimethylsiloxane). All of the data were obtained from the literature between 140°C and 180°C. Equation of state parameters for the polymers were obtained from reference 4. The maximum error between experiment and theory is about 10%.

For low molecular weight liquids, theory correctly yields the temperature coefficient of σ, or equivalently, the surface entropy, $-d\sigma/dT$. For polymer melts, theory consistently overestimates the surface entropy. This deviation is hardly surprising because we have ignored the confining effect of the interface on the conformational freedom of a polymer molecule. This effect should lower the surface entropy of a polymer liquid.

In summary, combining the LF model with CH theory yields a unified theory of surface tension applicable to non-polar and slightly polar liquids of arbitrary molecular weight. Without any adjustable parameters, calculated surface tensions are usually 10-20% lower than experimental ones over a broad temperature range. If $\bar{\kappa}$ is set equal to 0.62 for low molecular weight liquids and equal to 0.55 for polymers, much better agreement is obtained between theory and experiment.

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Experimental Methods of Migration Measurement

S. S. Chang, W. J. Pummer and L. E. Smith

The objective of this project is to measure the kinetics and maximum level of migration of low molecular weight materials (oligomers as well as antioxidants, plasticizers, stabilizers, and other additives) from polymers into its surroundings. This is a project sponsored by FDA to study the migration of indirect food additives from plastic food packaging materials to provide the technical basis for the regulation of plastic formulations to be used in contact with food.

Similar studies may also be applied to study the effect of low molecular weight materials on the mechanical properties and the durability of plastics which may cause failures in, for example, medical implant devices, shipping containers, and vinyl upholstery.

A variety of techniques are be used to study the diffusion-migration phenomena and the mechanisms that govern the diffusion processes. These techniques start with the direct observation of the migration phenomena by radioactive tracers, fluorimetry, gas chromatography, and other methods, pending on the migrating species and the sensitivity required. Additional studies include the diffusion constants obtainable through concentration gradient profiles by plasma oxidation and fluorimetry, vapor phase sorption and desorption studies and permeation studies. Solution parameters are also important in estimating the maximum level of migration through thermodynamic properties such as solubility, partition coefficient, and solvent-solute interaction parameters. Other factors that affect the migration, such as the morphology of the polymer, will also be studied.

In the past year, we have set up laboratories suitable for radioanalysis associated with tracer work. The reliability of the radioanalysis instrumentation was checked thoroughly and was verified against NBS SRMs. A laboratory for high sensitivity density measurement was also set up. Other laboratories for gas chromatography, inverse gas chromatography, fluorimetry, vapor sorption, and desorption studies are being set up.

In order to establish definitive data, we have used our well-characterized polyethylene as starting materials. To these materials we have added radioactive labeled low molecular weight oligomers. A system of octadecane and high density linear polyethylene have been studied this year. Three solvents, heptane, ethanol, and water, were used. In this system we find that no blooming of the added oligomer occurred. The Fickian behavior of diffusion was

obeyed only for a very short range. Migration is greatly enhanced by penetrating solvent. The initial diffusion constants is somewhat concentration dependent.

In order to correlate the diffusion-migration phenomena, direct migration studied are planned on other oligomer-polyethylene (HDLPE and/or LDBPE) systems in next year together with diffusion constant and thermodynamic parameter studies.

Transport in Crystalline Polymers

J. P. Colson and D. H. Reneker

The transport of polymer chains occurs at significant rates in polymer crystals as evidenced by the increase in the thickness of lamellar crystals that is observed by low angle X ray diffraction or by measurement of the longitudinal acoustic mode frequency. Such transport processes may lead to changes in mechanical behavior, dimensional stability, permeability, durability or other properties critical to the use of crystalline plastics. Improved experimental methods are being developed to characterize processes that are involved in molecular transport. The infrared spectrum of partly deuterated polyethylene contains a band which is assigned to trans-gauche bond sequences. From measurements of the intensity of this band as a function of temperature, the concentration of trans-gauche sequences in polyethylene can be inferred. The observed increase in the concentration of trans-gauche sequences in the temperature range at which significant molecular transport rates are observed suggests that the thermal generation of such sequences is involved in the molecular transport processes. This suggestion is bolstered by calculations of the conformational changes in the molecule needed to create trans-gauche bond sequences, and by observation of a decrease in the intensity of the longitudinal acoustic mode in the temperature range in which transport occurs.

Measurement of Transport in Polymers by IR Spectroscopy

··J. C. Philips

Due to the increasing use of polymers as barrier materials and often under varying conditions of load, it is of importance to study these materials as to transport and mechanical behavior. The objective of this work is to define as thoroughly as possible the use and limitations of the IR absorption technique to the study of transport properties. The interdependence of transport properties morphology properties is also an important concern.

The IR technique may only be applied adequately to a compatible polymer/vapor system, i.e., the vapor should have an absorption frequency of interest in a region where the polymer has negligible absorption. Once a system has been chosen, the transport properties (e.g., sorption and diffusivity) are obtained from the change in absorption intensity (absorbance) with time. In order to convert time-dependent IR data to time-dependent weight data, calibrations of equilibrium (excess) weight per weight of film and absorbancy versus pressure must be obtained, i.e., a calibration of absorbance versus excess weight per weight of film is determined.

The results of this particular study may be summarized as follows:

1. An IR cell was designed and constructed for measuring transport and mechanical properties. Films may be characterized as to sorption, diffusivity, permeability (P=SD), stress and strain levels.

2. Quartz spring measurements at 30°C have been done on the following systems:
   a. A-33C/ethyl acetate   (A-33C=Copolymer: PCTDE/PTFE)
   b. PE/methylene chloride
   c. PVF /ethyl acetate
   d. PS/methyl alcohol   (PS=polystyrene)
   e. PE/ethyl acetate   (PE: low density and
                               biaxially stretched)

Pressure dependency of sorption was done for PVF /ethyl acetate, PE/ethyl acetate and PS/methyl alcohol.

3. Infrared measurements at 30°C have been done on the following systems:
   a. A-33C/ethyl acetate
   b. PVF /ethyl acetate
   c. PS/methyl alcohol
   d. PE/ethyl acetate
   e. crosslinked PE/ethyl acetate

4. Stress/strain data have been done for PE up to a strain level of approximately 60%. Similar data have also been obtained for A-33C up to a strain level of approximately 5% at various temperatures.

5. Transport and stress relaxation data for PE/ethyl acetate as a function of elongation and pressure have been done. The results show the effect of cyclic sorption/desorption on stress relaxation and the effect of strain on sorption and diffusivity.

Polymer Structure Control Methods for Dielectric Design and
Durable Performance

Trends in dielectric application of polymers include use of
higher working voltages in electrical apparatus and transmission
lines to conserve materials, save space, and reduce weight. This
work provides manufacturers (polymer manufacturers, film fabricators,
transducer manufacturers), trade associations (EPRI), and government
agencies (DOE, DOD) with data, measurement methods, and concepts
which identify limitations in polymer performance traceable to
manufacturing practices. For example, steam curing of extruded
polyethylene insulated cables results in lifetime limiting voids
and inclusions. With a trend toward increased use of underground
transmission of electric power, improved insulation performance is
required. Data and recommendations from this work go directly to
cable manufacturers and funding organizations (*i.e.*, EPRI, DOE) who
are able to specify and require manufacturing changes leading to
improved products.

Other trends are new, rapidly growing applications of polarized
polymers as pyro- and piezoelectric transducers. Transducer manu-
facturers as well as private and government transducer users (DOD,
EPA, HEW) need reliable information connecting polymer structure and
polymer performance for the design of improved transducers. This
work will help transducer material-and device manufacturers design
and develop commercial polymer transducers for use in health and
safety applications (pulse monitors, therapeutic and diagnostic
sound measurements, auto crash sensors, prosthetic fitting devices,
non-toxic antifouling coatings, mine disaster warning devices)
and in the areas of national security (microphones, hydrophones,
intrusion detectors, ultrasonic and infrared imaging devices, fusing
devices, etc.). Important scientific opportunities of this work in-
clude breakthroughs in understanding the basic factors in electrical
failure of polymers and discovery of novel measurement methods which
are becoming possible with newly developed polymers. For example,
this work attempts to show how polymers interact with electronic and
ionic charges, how structure control can minimize adverse effects of
these charges, and how polymers can be modified to optimize piezo-
electric, pyroelectric, and semi-conducting properties.

Polymer Insulation for Superconducting AC Power Transmission Cables

F.A. Khoury, F.I. Mopsik, S.J. Kryder and L.H. Bolz

This project, sponsored by and carried out in collaboration with Brookhaven National Laboratory (BNL) with DOE funds, is part of a program for evaluating the suitability of various types of polymer films for use (in tape form) as the electrical insulation in high power superconducting AC transmission cables operated at 6K-9K. Such cables, in which the superconductor is Nb_3Sn, are currently under development at BNL. Among the guidelines used for selecting the insulation for such cables is that the dielectric constant (ε) should be 2.5 or less, and that the dielectric loss (tan δ) should preferably not exceed 20×10^{-6} at the cable operating range and 60 Hz.

This subtask is primarily concerned with the measurement of the dielectric properties (ε, tan δ) of polymer films at cryogenic temperatures. These measurements, for which NBS has a unique instrumental facility, are coupled with studies of aspects of the fine structure of the films in an effort to determine the influence of various structural parameters (*e.g.*, crystallinity, molecular orientation, voids) on the dielectric properties of the films. In addition to determining whether specific types of commercially available films meet the established criteria for dielectric properties, these studies are aimed at providing data relevant to the design and production of films exhibiting optimum dielectric properties for the intended end use. In a less extensive effort, the compressibility of the polymer films is measured. This latter feature is among others, relevant to the determination of the optimum conditions (*e.g.*, tape tension) necessary for winding the films (slit in the form of tapes) around the cable core, so as to yield a cable exhibiting appropriate flexibility for winding onto storage drums 10 ft. in diameter.

During FY1978 a comparative study of the dielectric loss characteristics of six commercial polypropylene films before and after annealing at 408K was completed. Both ε and tan δ were measured at temperatures between 4.2K and 323K. The densities of the films as well as the nature of the crystalline orientation(s) in the samples were determined. All the samples studied were suitable with respect to the above mentioned criterion for the dielectric constant. Significant differences in tan δ were observed, however, in the temperature range of prime interest (4K-10K) among the unannealed films. In some cases the value of tan δ in that temperature range (4K-10K) exceeded 20×10^{-6}, whereas in others tan δ was as low as 5×10^{-6}. It was established that the magnitude of tan δ for polypropylene at these low temperatures is influenced by the contributions to tan δ resulting from the following two superposable features: (a) The

presence of antioxidant in the films which gives rise to a loss peak below 4.2K where high temperature tail spans the range of 4K-10K. (b) The manifestation of a broad loss peak at 30K (of as yet unknown origin) whose low temperature tail also spans the 4K-10K range.

It was found that the loss peak at 30K is suppressed by annealing the polypropylene at 408K, which also results in a decrease of tan δ at 4K-10K. No direct correlation was found between the intensity of that peak, as manifested in unannealed samples, and the degree of crystallinity of the samples which varied between 35%-67%. Experiments aimed at determining the origins of the dielectric loss peak at 30K are currently being planned. It is of interest to note that the occurrence of a mechanical loss peak of unknown origin at 30K was observed several years ago in a study of the dynamic mechanical properties of polypropylene.

An experimental survey was also carried out of the dieletric properties of polypropylene-polyurethane laminates at cryogenic temperatures. These laminates consist of either two or three layers of polypropylene film separated from one another by a layer of polyurethane. It was established that the contribution of the polar polyurethane to dielectric loss at 4K-10K is far from negligible and that the volume fraction of polyurethane must be carefully controlled and kept sufficiently low if the criterion for tan δ ($<20 \times 10^{-6}$) is to be met. A potential problem concerning the use of the laminated films as the electric insulation in superconducting cables was identified in some of the earlier laminates which were studied. The polyurethane layers contained numerous voids ranging in lateral dimensions from a few micrometers to several hundred micrometers. Such voids are likely to serve as sites for the manifestation of discharges leading to a progressive degradation and ultimate breakdown of the electric insulation. Accordingly, BNL has requested the manufacturer of these experimental laminates to alter their lamination process so as to eliminate the voids.

Polymer Tape Insulation for Oil Impregnated AC Power Transmission Cables

F. A. Khoury, F. I. Mopsik, S. J. Kryder and L. H. Bolz

Oil impregnated paper (cellulose) tape has been for many years one of the most commonly used types of electric insulation in high power AC transmission cables. The current and projected needs for more efficient power transmission systems have elicited considerable interest in the development of oil impregnated or oil filled cables operated at 700Kv-1000Kv in which polymer tape insulation will be used instead of the conventional paper tape which is unsuitable because of its large dielectric loss.

In a project, sponsored by Brookhaven National Laboratory with DOE funds, a program has been initiated in the Polymer Science and Standards Division for evaluating the suitability of various types of polymer films as replacement for paper tape in high voltage oil impregnated AC transmission cables. The goals of this study are: (a) The measurement of the dielectric constant and dielectric loss of candidate films between 273K and 423K. (b) The determination of the dependence of the dielectric loss on the fine structural characteristics of the films. (c) The specification of the dielectrically most suitable type of film for the intended end use.

Accomplishments for FY 1978: A special dielectric cell for measuring the dielectric constant and dielectric loss of polymer films in the temperature range 293K to 423K was designed and built. Measurements on polypropylene films have been initiated.

Porous Polymer Tapes for High Voltage Transmission Cables

A. J. Bur, M. G. Broadhurst, and W. P. Harris

Existing underground high voltage transmission cables are made with an insulation consisting of layers of paper tape saturated with a dielectric oil. This system has proved to be adequate for voltages up to 325 kV. At higher transmission voltages dielectric dispersion in the paper produces unacceptable dielectric losses. In the foreseeable future electrical transmission at voltages higher than 325 kV will be necessary and a substitute for paper is being sought. A polymer material is a logical choice. Some work on solid polymer films has been carried out in the past but the permeation of oil throughout the lapped tapes and encapsulated voids in the films are problems which impede other uses of solid films. It is possible that porous polymer tapes can overcome these problems through improved oil permeation and decreased occurrence of unfilled voids.

The Electric Power Research Institute (EPRI) is supporting this porous polymer tape project. The objective of the project is to establish a screening program by which candidate materials can be tested and a judgment made regarding their suitability as cable insulation. The screening program which we have developed consists of criteria for physical properties which the tapes must have and a description of the tests by which these physical properties can be measured. On the test schedule there are 21 tests to measure the following physical properties: dielectric constant, dielectric loss, dielectric breakdown, softening temperature, mechanical moduli in three directions, coefficient of friction, yield strength, fracture strength, solubility, creep and recovery, swelling, and degree of void filling.

With the exception of the degree of void filling and solubility tests, a description of these tests was obtained from literature sources and ASTM test schedules. The degree of void filling and solubility tests are being developed through our own laboratory experience. For these two tests, we are using a method which is designed to measure the bouyant force of a sample immersed in a dielectric oil.

To measure the degree of void filling, the density of a porous sample is first measured in a calibration fluid which is chosen because of its efficient permeation into the material being investigated. (For example, heptane is known to permeate into polyethylene filling microvoids in the material.) It is assumed that this calibration fluid fills all pores and voids so that the true material density can be obtained from the bouyant force measurement. A bouyant force measurement is then made for the sample immersed in a dielectric oil. The difference between the immersed-in-oil density and the calibration density is proportional to the volume which is unfilled by the dielectric oil. Solubility can be measured by weighing the dry sample before and after immersion in the fluid being tested.

Oil permeation into the sample is a common conditioning step in many of the dielectric and mechanical tests which must be carried out in oil. Temperature and vacuum cycling are often necessary in order to increase the permeation of oil and decrease the unfilled void volume. The bouyancy measurements are being developed to observe these conditioning parameters.

ASTM Activities

W. P. Harris

ASTM Committee D-9 on Electrical Insulating Materials met three times in this period:

> Oct. 25-27, 1977, in Philadelphia
> Mar. 14-16, 1978, in Atlanta
> June 26-28, 1978, in Boston

Mr. Harris, Chairman of D-9 and of its Executive Subcommittee, attended and chaired these meetings and also took part in the activities of several of the Subcommittees.

At each meeting, 20-30 standards are balloted for revision or reapproval. Because ASTM now requires every test method to contain a section on sampling and one on precision and accuracy, most of the existing standards require revisions. This has resulted in an unusual amount of work for all of the technical subcommittees and especially for the Editorial Subcommittee, which must approve all revisions.

Conversion of all standards to SI units is a time-consuming and tedious chore, and is also a source of some controversy.

The perennial problem of achieving adequate attendance and participation received special attention at the Philadelphia meeting. As older members retire and drop ASTM activities, some companies are not sending replacements. In D-9, this problem has been especially acute in S/C 9 on Mica Products, S/C 5 on Ceramic Products, S/C 1 on Insulating Varnishes, Powders and Encapsulants. Discussions with ASTM HQ staff has led to organization of a workshop on this topic to be held Sept. 25 and 26, 1978, at ASTM HQ in Philadelphia, as part of the Biennial Conference for ASTM Technical Committee Officers. Mr. Harris will attend and participate.

The Subcommittee on International Standards continues very active, with many documents to review and U.S. position statements to be prepared. D-9 supported, and shared support for several delegates to the meetings in June 1978 of IEC TC 15C in Florence, Italy.

The new Section on Electrical Ignition in the S/C on Electrical Tests prepared a new standard on this subject, which is now in final ballot stages.

At the June, 1978 meeting in Boston, another new section, on Electrical Safety, was formed in the S/C on Electrical Tests.

Fabrication of Piezoelectric Polymer Film

J. M. Kenney and M. G. Broadhurst

The fabrication of polar films of poly(vinylidene fluoride) has become of increasing importance because these films are used as piezoelectric and pyroelectric transducers having an unusual combination of properties. Although the electrical behavior of this material has been studied for a number of years, there has been no systematic attempt to isolate the combination of variables encountered in the poling (polarization) process which will optimize the piezoelectric and pyroelectric activity and durability. Some of these variables are: poling voltage (field strength), poling and annealing times, poling and annealing temperatures, electrode material(s), film thickness, and mechanical orientation. For practical applications, the film must be of highest activity over extended use, so that stability of activity is highly important.

For this project, we initially investigated temperature dependence at a single field strength. Since it appeared that higher fields could be applied at lower temperatures, we tried poling at room temperature, and obtained very high activities after poling to breakdown using fields up to 500 MVm^{-1}.

(12.5 kV across 25μm film). Previous work, at NBS and elsewhere, had indicated that corona poling with high fields at room temperature would yield comparable activities, but this was the first time that such fields had been applied to fully electroded samples at room temperature. Erratic breakdown behavior led to a study of time-to-breakdown as a function of field. It was found that there was an order-of-magnitude change in time-to-breakdown for each 100 MVm^{-1} change in field. Breakdown times obtained ranged from a little over two minutes at 420 MVm^{-1} to over a day at 160 MVm^{-1}. From this data it was concluded that the maximum poling field at which breakdown should not occur, can be closely approximated by the relationship $E_{(max)} = 600 - 100 \log t$. $E_{(max)}$ is the maximum field in MVm^{-1}, and t is the poling time in seconds.

Using this relationship, poling along the breakdown line and below it is currently under way to obtain activity as a function of both field and poling time. From this, contours of equal activity will be plotted to identify the optimum poling conditions at room temperature, using aluminum and other electrodes. Further work will be needed to include variation of temperature and sample thickness. Further studies are underway to determine stability differences and to determine optimum poling conditions for maximum stability. This work is being supported by the Naval Undersea systems Command.

Charge and Polarization Distributions

A. S. DeReggi, M. G. Broadhurst and S. B. Lang (guest)

A thermal pulse method of measuring the distribution of space charge or polarization across the thickness of dielectric films has been under development at NBS for the past several years. Progress has been made in the understanding of the type of information which can be obtained by the thermal pulse method and how to extract this information. This theoretical work was published this year.

When applied to piezo and pyroelectric polymers, the thermal pulse method has shown that poling does not occur uniformly across the thickness, in general, probably because of the presence of electric charges in the bulk of the film during polarization. In certain polymers such as polyvinylidene fluoride and in copolymers with tetrafluoroethylene, polarization under low poling fields (in short times) occurs first near the anode and progressively spreads across the entire thickness at higher poling fields, temperatures and times. In the case of polyvinyl fluoride the opposite situation obtains. Poling occurs at low fields at the cathode and spreads towards the anode at higher fields, temperatures and times. Theoretical work is in progress to understand the charge transport processes involved and the possible role of polymer-metal work function differences.

When applied to good insulators such as polyethylene, the thermal pulse method has shown that applied fields charge these polymers also. The charge distributions tend to be concentrated near one surface. However, there is a suggestion based on the behavior of the piezoelectric polymers (which are somewhat poorer insulators than polyethylene) that given sufficiently long term exposure to a voltage, space charge build-up and electric field distortion occur. Work on insulators with small charge concentrations requires a considerable upgrading of the thermal pulse apparatus. Consideration is presently given to going from a flash lamp to a CO_2 laser to obtain both intensity increases and shorter thermal pulses, both of which are needed to study narrowly concentrated charge distributions. Work in progress is aimed at establishing whether slow charging of insulators could play a decisive role in dielectric failure of electric power cables.

Professor Sidney Lang a pyroelectric expert from Ben Gurion University in Israel is spending two months at NBS to colaborate in the study of polarization and space charge in polymers.

Ultrasonic hydrophones

A. S. DeReggi, J. M. Kenny, and S. C. Roth

Because the acoustical impedances of polymers and that of water are similar, it is possible to make polymeric hydrophones which are nearly non-perturbing of the acoustical fields they measure. The Bureau of Radiological Health needs miniature ultrasonic probes made with piezoelectric polymers for characterizing the spatial distribution of the acoustical intensity radiated by ultrasonic medical transducers used for thermotherapy. NBS has provided BRH with consultation, development work under a funded Interagency Agreement, and has also collaborated with a guest worker (Gerald Harris of BRH) to perfect the hydrophone. The hydrophone consists of a polymer sheet held taut by a hoop of large diameter (10-20 cm) compared to the diameter of the acoustical radiation field to be probed and has a 1 mm diameter, piezoelectrically sensitive area confined to the center of the sheet. Electrical connections to the small sensitive area are accomplished by vacuum deposition of thin-film metal leads. This ultrasonic probe has adequate responsivity (-230 dB re 1 V/P_a) extending to at least 10 MHz, and alters the radiation field by less than 1/2 dB up to 1 MHz when the probe is inserted in the beam. Personnel concerned with hydrophone calibration methods at the Naval Research Laboratory and at John Carroll University have become interested in this NBS-developed hydrophone, and have expressed a desire to use it in their work. BRH plans to exploit the broadhand detecting capabilities and the non-perturbing feature of the hydrophone in their future work.

The NBS polymeric hydrophone work was described in a news item in the Medical Devices Newsletter and will be published elsewhere in the forthcoming year.

Piezoelectric Polymer Deposition

S. C. Roth and S. Edelman

This work, sponsored by the U. S. Army Research Office, is aimed at developing piezoelectric-polymer-coated metal surfaces such as the inner surfaces of large caliber fused shells. The initial phase involved various methods for depositing uniform thin films and subsequent work involved methods for making the film piezoelectrically active.

Both thermal evaporation and plasma sputtering were shown to be unsuccessful as means of depositing films using available equipment. For this work a vacuum evaporator, used for depositing metallic electrodes, was used. Fixturing included two metal plates separated by a gap of approximately one centimeter. High voltage feedthroughs were connected to each plate and an arc lamp was placed to act as a heat source for one of the plates. Both plates also had insulated thermocouples imbedded to monitor the temperature. Various combinations of constant electric fields and pulsed fields were applied while the source plate, which had a thick polymer coating was heated up to temperatures approaching decomposition values. In several cases a deposit was formed on the target plate but it was never thick enough to be useful.

Currently work is being done with fused powder films of PVDF and PVDF-TFE copolymer. By fusing a coating of electrostatically charged polymer powder on a metallic substrate a fairly thin, uniform film can be formed. Five centimeter diameter metal disks each with a smooth chrome plated surface were used as substrates. The chromed surface is coated with a layer of polymer powder using an electro-static powder spray gun. The polymer powder is then fused into a film by heating the coated substrate disks in an oven at 300°C. One batch of nine samples of the PVDF-TFE was made by spraying and fusing three separate layers in order to maximize uniformity of the coating and build up the thickness. These films adhered well to the metal and five had a thickness of approximately 62μm and four had a thickness of approximately 130μm. These samples were poled with a corona discharge, at fields up to 3 MV/cm. This corona poling technique, which requires only one backing electrode (in this case the metal substrate disk) produced films with a maximum piezoelectric coefficient of 4.3 pC/N and a pyroelectric coefficient of 1.0 nC/cm K. Current efforts are aimed at increasing the reproducibility of this process.

swept out of the material by the applied field), at higher temperatures (where the removal of space charge is faster because of increased conductivity) and at higher voltages (where the field due to space charge is a small fraction of the applied field). All of these qualitative predictions are in accord with experiment and we are presently developing the theory of this space charge effect more completely in order to design appropriate experiments for measuring it directly. A thermal transient instrument is being used in our laboratory for this measurement of space charge. This part of the work is developing satisfactorily.

One of the most significant advances is the discovery that the antipolar formII crystal phase of PVDF can be made piezoelectric. X-ray evidence indicates that an electric field of about 1 MV/cm induces a new polar crystal phase with the same unit cell dimensions and apparently the same tgtg' chain conformation. At much higher electric fields the crystal is transformed to the polar form I which involves not only a change in cell dimensions but also a rearrangement of the chain to an all trans conformation. The latter changes are clearly seen in both x-ray and ir spectra. These results have been reported in ONR Technical Report No. 8 and will appear in the October 1978 issue of J. Appl. Phys.

Plasma poling or corona poling was thought to allow the application of higher electric fields than were possible by applying a voltage directly to metal electrodes evaporated onto the polymer film. However, recent work on a related project leads to the conclusion that so-called "conventional poling" can be accomplished at fields equal to those of corona poling if precautions are taken to avoid breakdown in air by immersion in a dielectric fluid. Poling in plasmas of different gases was not pursued except in special cases where evaporated electrodes are undesirable.

Information about the polarization distribution across the thickness of a piezoelectric polymer film can be obtained using the thermal pulse technique developed by R. E. Collins while he was a guest worker at NBS. A scheme for analyzing the data using Fourier analysis was reported in ONR Technical Report No. 6 and was published in Phys. Rev. Lett. 40, 413 (1978). The digital cartridge recorder which was acquired with ONR funds required several modifications before it was acceptable and it is now functioning properly. Dr. Sidney Lang, a guest worker from Ben Gurion University in Beersheva, Israel, is presently collaborating with us to study polarization distribution in PVF.

During the past year the basic research on piezoelectricity in polymers at NBS has been carried out at a level of two man years, jointly supported by NBS and ONR. The total effort in piezoelectricity involves an additional three man years which is directed more to research on applications and measurement problems which require the unique advantages of polymer films. The following results were obtained during 1978.

A model for piezo- and pyroelectric activity has been developed specifically for thin lamellar crystallites dispersed in a non-crystalline matrix--a morphology common to all semicrystalline polymers. The origin of the electrical response to mechanical or thermal stress arises principally from volume changes as opposed to changes in dipole moment. Accumulation of space charges at the crystal liquid interface has been included and results indicate that their contribution is small. Exact comparison between theory and experiment is limited by the lack of reliable data on some of the material properties but reasonable estimates lead to the conclusion that the experimental results can be well accounted for by the model. These results have been submitted in ONR Technical Report No. 9 and will be published in J. Appl. Phys. in October 1978.

A preliminary model for the switching of dipole orientation in an applied electric field has been developed to account for the poling of polymer crystals. Basically, it is a two-site model (dipoles aligned with or opposed to the field) in which the energy difference between the two sites is a function of the relative population of the two sites. This leads to a cooperative effect much like order-disorder transition theory for alloys. A critical field for poling is predicted for PVF which is in line with that which is experimentally observed. The material parameters required for the predictions are known better for PVF than for PVDF and we are currently obtaining the necessary poling data to critically check the theory. The theory is presented in a manuscript to be published in a book on electrostatics.

The problem of the distribution of space charge in PVDF during poling is developing slowly as expected in last year's proposal. We have a large amount of new data which shows that at low poling fields, the PVDF polarization is greatest at the positive electrode and in PVF the polarization is greatest at the negative electrode. Our explanation for these effects is that there is a net negative space charge in PVDF and a net positive space charge in PVF. We believe these charges arise because the PVDF acts as an electron acceptor and the PVF as an electron donor with respect to the aluminum electrodes we usually use. The distortion in the applied field due to the charges causes the field to be highest at the electrode of sign opposite that of the space charge. This distortion is less at longer poling times (after the space charge has been

Structure and Performance of Piezoelectric Polymers

G. T. Davis, M. G. Broadhurst, and J. E. McKinney

The objectives of this subtask are:

1) To study molecular motions, structural changes, and electrical properties which are associated with the process whereby polymers are made piezoelectric,

2) To develop a suitable theoretical model for piezoelectricity in polymers--especially semicrystalline polymers, and

3) To investigate how to optimize and predict piezoelectricity with respect to both initial activity and long term stability.

Poly(vinylidene fluoride) continues to be the polymer of greatest interest in piezoelectric and pyroelectric investigations. There is growing interest in both basic and applications research in academic and industrial laboratories. For example, there were 10 papers presented at an NBS-organized symposium at the 175th ACS meeting in March 1978 and 12 papers presented at the American Physical Society the same month. An article in the NBS Dimensions magazine in February 1978 followed by reports in Science [200, 1371 (1978)] and Materials Engineering [May 1978] have resulted in many requests for information and consultation with NBS scientists.

The creation of an electric-field induced polar form II followed by conversion to polar form I at higher fields lends further support to our original model of aligned dipoles within the crystalline phase as the basis of the polarization in PVDF. Space charges within the polymer are thought to be important in determining the electric field distribution during the poling process. There are some investigators who assign them the major role in piezoelectric activity.

Our research suggests that experimentally obtainable PVDF activity is about one half its theoretical maximum. This activity remains below that obtainable with good ceramic materials so that most important applications for the polymer will be ones which require its unique properties of toughness, flexibility, ease of fabrication, broad-band response, and mechanical impedance. Two recent U. S. commercial products, a heat scanner for use in fire detection and a passive intrusion detector, use the pyroelectric response in PVDF. Device manufacturers are actively using NBS-developed technology to produce devices and we are expecting a research associate from a microphone company to work with us next year in that area. In addition, we have a guest worker from the Bureau of Radiological Health who is applying NBS-developed hydrophones to calibration of ultrasonic medical devices and a guest worker from Israel who is an expert in pyroelectricity.

Polymer Stress Gauge for Intaglio Printing Press

S. C. Roth, J. M. Kenney, and S. Edelman

This work, which is supported by the Department of Treasury, Bureau of Engraving and Printing, involves the development of a gauge to be used to study the behavior of the presses used to make paper money. At present there is no way to monitor the presses, and this deficiency results in component failure and unscheduled down time. The study is divided into three phases. Phase I is the development of a suitable gauge. Phase II involves calibration of the stress measuring units under the conditions which occur when the press operates. Phase III consists of instrumenting other presses.

The piezoelectric properties of poly(vinylidene fluoride) (PVDF) make this material ideally suited for two reasons. First, the gauge must be thin enough so that it does not interfere with actual printing. Second, the gauge must be flexible and durable enough to withstand the large pressure transients generated during printing. The gauge consists of a long strip 80 cm long and 7 cm wide. There are four active areas, each 2mm wide and 13.8 mm long, which are displaced latitudinally along the length of the gauge. All four sensitive areas are connected together electrically but separated spacially so that when the printing press drum rotates the pressure pulses are separated in time.

The gauge is made of two sheets of 12μm thick PVDF sandwiched together to give a completed gauge thickness of between 30 and 40μm. The single output connector is attached to a small FM transmitter mounted on the side of the drum. During the past year four visits have been made to the Bureau of Engraving and Printing to try out various gauge designs. During the course of the visits several problems were encountered. The gauges constructed for the first visit were made from two layers of 25μm thick PVDF, epoxied together, with the exterior surfaces covered with a vacuum evaporated aluminum shield electrode. They were glued to the outer fabric layer of the printing drum so that they came in direct contact with the engraved plates during printing. The main difficulty encountered was keeping the FM telemetry system in tune. Also, the quality of the printed money was not acceptable due to the presence of the gauge on top of the pressure pad. On removing the gauge the shield electrode peeled off thus effectively destroying the gauge. As a result of this visit, some changes were made in the telemetry electronics and a new gauge was constructed using 12μm thick PVDF for the two active layers. After bonding the active layers together and depositing the shield electrode, two protective layers of 9μm thick polymer were epoxied over the shield electrodes to protect them during removal of the gauge after testing. On the second visit to the Bureau of Engraving and Printing this gauge was placed between the outer fabric

and the first cardboard layer of the pressure pad. Although the output pulse level was sufficiently high to discriminate from the noise, the level did not stay constant. On removing the gauge, it was noted that the protective layer had delaminated. Evidently the aluminum shield electrode evaporated on the outside of the gauge did not adhere well to the polymer. Consequently, the protective layer, which was epoxied over the shield electrode, was not adequately bonded. For the third visit, since the gauges were to be placed between cardboard layers instead of being glued to the outer fabric layer, no protective film was added during construction.

After initial placement a usable signal was obtained similar to the signal photographed during the second visit. In addition to the desired signal, there was considerable noise present. During the course of the run various antennae placements were tried with the final result being that the antenna was mounted on a cardboard strip projecting out from the edge of the drum. Also, it was noticed that, even without the gauges connected to the transmitter, the received signal had large noise spikes. In an effort to correct this, the transmitter was removed and the internal components were potted in epoxy. Also, a rubber pad was placed under the transmitter when it was mounted on the drum.

Unfortunately, no further results were obtained. Both gauges had developed an open circuit so that no signal was reaching the transmitter. The cause of this unusual failure was not apparent as neither gauge visually appeared to be damaged. On further examination it was found that, although the external aluminum shield electrode appeared undamaged, it no longer formed an electrically continuous path.

When a shield electrode was reapplied, it was discovered that the gauges had depolarized and become inactive. The gauges had been poled under less than maximal conditions so that the output due to the large pressure pulse would not saturate the telemetry electronics. Evidently such weakly poled films are much more easily depolarized. To test this hypothesis, several samples were run on the printing press for approximately one hour. The samples which had been weakly poled showed approximately a 25% decrease in activity while the samples that had been well poled and then annealed under short circuit conditions at 80°C for one week showed no change in activity from the after-annealing value to the value obtained after running them in the press.

Currently, gauges are being made using just two 12μm thick layers of PVDF with the active areas poled under near maximum conditions. The gauge then has a 10,000Å thick layer of indium applied as a shield electrode after which it is annealed at 80°C.

Development of Piezoelectric Polymer Stress Gauges for Rock Studies

S. C. Roth and S. Edelman

The United States Bureau of Mines requested that the National Bureau of Standards design and construct transducers needed to solve a special measurement problem. This request was based on results obtained by BM from four piezoelectric polymer stress gauges which were supplied by NBS to the Denver Mining Research Center to be used in measuring noise from rock specimens during mechanical loading. The success of those gauges suggested that gauges of similar construction could be useful for two additional purposes: (1) to detect and locate the source of acoustic emission in rock specimens, and (2) to monitor changing acoustic transmission characteristics of laboratory rock specimens as a function of stress history. In general, the gauges are required to make dynamic pressure measurements at the interface between irregular-shaped, moving objects. The fact that the polymer gauge conforms to the space between irregular surfaces makes it unique for use in this application, for which commercially available ceramic transducers are unsuitable.

To accurately locate the sources of rapidly occurring acoustic noises in a laboratory rock specimen, the transducer must be highly damped with a vibrational decay time of approximately 10 to 20 microseconds, small in size (approximately 2 to 3 mm in diameter and less than 0.1 mm thick), and have a flexibility such that several transducers can be clamped to the cylindrical surface of an NX size specimen (about 17.5 cm long and 5.6 cm in diameter) with the use of a flexible pressure jacket.

To monitor the effect of changing stress on the acoustic wave transmission characteristics of a laboratory rock specimen, it is necessary to detect these waves as they pass through the specimen during changing load conditions. To accomplish this, the transducer must be able to withstand a high static load and still respond to the dynamic pressure changes at the interface between two adjoining surfaces. The transducer must be thin compared to the wavelengths of the noise being detected.

At present four different sets of gauges are being constructed. There are three sets of gauges which consist of single active areas with diameters of 5, 3.5, and 1.6 cm, respectively. The fourth set of gauges consists of a 16 element array of 2 mm diameter active areas deposited on a single sheet.

Automated Dielectric Measurements

F. I. Mopsik, S. J. Kryder, and S. C. Roth

An automated dielectric spectrometer is being constructed to maximize speed and accuracy of dielectric data aquisition. The spectrometer records the transient response of a dielectric sample in real time and using numerical transforms, automatically determines the dielectric contant and loss of a sample over a frequency range from about 10 KHz to 0.001 Hz or below.

All the components needed for the dielectric spectrometer have now been procured. This instrument is intended to have loss resolution in tan δ of 10^{-5} so that it will be of sensitivity comparable with typical bridge measurement. Time savings will be an order of magnitude better than previous instruments.

One completed component is a programmable, triggerable clock that will enable data sampling at the optimum and variable rates needed in determining the transient response with a maximum uncertainty of $1 \times 10^{-7} + 100$ ns. Another critical component, currently under construction is a dual output step function generator capable of generating $\pm$ 100 V steps that have a 10µs rise time and are matched to one part in 10^{-5}. This is needed so that the constant capacitance term can be subtracted out by a standard capacitance, enabling full analog to digital resolution of the transient response thus realizing the required resolution. The adequacy of the step generator has already been demonstrated and completion is expected shortly.

Investigation of numerical transforms have been made and ways have been found to quantify errors analytically. This step is important for maximum accuracy. A Tandberg digital recorder was interfaced to the Interdata computer and the transient recorder so that experimental data can be recorded on data cartridges and later pluged back into the computer for automated analysis and presentation. The physical problems have been solved and a program to transfer the data is being debugged. The program is particularly applicable to the transient data from the thermal pulse measurement of polarization and charge distributions in polymers.

Support work that has been completed includes a graphics program suitable for displaying the results of either the transient spectrometer or the thermal pulse experiment graphically to aid in the interpretation of the experiments. Also several real-time programs for data acquisition that can read BCD instruments, clock data and determine measurement equilibration have been successfully tested. The resistance vs. temperature characteristics of polymer

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Processing, Rensselaer Polytechnic Institute, Troy, NY (1977)

"An Evaluation of Wood Pulp Paper Durability"
E. L. Graminski and E. E. Toth
Progress Report, NBSIR 78-1417 (1977)

"Problems and Theories of Polymer Crystallization"
I. C. Sanchez
J. Poly. Sci., 59, 109-120 (1977)

"The Disciples of Eugene W. Skinner: Philander B. Taylor and George M.
Hollenback"
G. C. Paffenbarger
Operative Dentistry, Vol. 2, No. 4, (1977)

"Adhesive Bonding of Various Materials to Hard Tooth Tissues: XIII
Synthesis of a Polyfunctional Surface-Active Amine Accelerator"
J. M. Antonucci and R. L. Bowen
J. Dent. Res. $\underline{56}$(8), 937-942 (1977)

"Solubility of $Ca_5(PO_4)_3OH$ in the system $Ca(OH)_2$-H_3PO_4-H_2O at 5, 15, 25,
and 37 °C"
H. McDowell, T. M. Gergory, and W. E. Brown
J. of Research NBS-A. Physics and Chemistry, $\underline{81A}$ Nos. 2 and 3, (1977)

"Longitudinal Acoustic Modes of Polytetrafluoroethylene Copolymers and
Oligomers"
J. F. Rabolt and B. Fanconi
Polymer, $\underline{18}$, 1258-1264 (1977)

"Henry's Law and Diffusion Constants of Vinyl Chloride in Poly(vinyl
Chloride) at High Temperature"
D. W. Brown and R. E. Lowry
J. of Poly. Sci., $\underline{15}$, 2623-2639 (1977)

"Uniaxial Extension and Compression in Stress-Strain Relations of Rubber"
L. A. Wood
J. of Research 82, No. 1, (1977)

"New Method Evaluates Coupling Agents Bonding Polymer to Tooth Mineral"
W. V. Loebenstein and J. W. Kumpula
J. Dent. Res., $\underline{56}$, (10): 1219-1226 (1977)

"An NDT Method Using Piezoelectric Polymer Transducers and Computerized
Vibrational Spectroscopy"
D. H. Reneker, S. Edelman, A. S. DeReggi and D. L. Vanderhart
NDT International (1978)

"Annealing of Drawn Crystalline Polymers"
A. Peterlin
Polymer Engineering and Science Vol. 18, No. 6 (1978)

"Optical Microscopy as Used in Unorthodox Ways"
C. P. Saylor
SPIC, Vol. 108, Optics in Security and Law Enforcemnt (1977)

"Piezoelectric and Pyroelectric Polymer Sensors"
S. Edelman
Report on Sensor Technology for Battlefield & Physical Security
Applications, Fort Belvoir, Virginia (1977)

"Surface Chemical Modification of Hard Tissues, I. Bone"
G. M. Brauer, D. J. Termini and S. M. Levy
J. Dent. Res. Vol. 56, No. 6, (1977)

Invited Talks

"Additive Migration from Polymer Films"
ASTM Committee F-2 (Flexible Barrier Materials) Technical Seminar on
Analysis of Plastics Food Packaging Materials, New Orleans, Louisiana
I. C. Sanchez
March, 1978

"Phase Transition Behavior of the Isolated Polymer Chain"
APS National Meeting, Washington, D.C.
I. C. Sanchez
March, 1978

"Surface Tension Theory of Pure Liquids and Polymer Melts"
APS National Meeting, Washington, D. C.
I. C. Sanchez and C. I. Poser
March, 1978

"Additive Migration from Polymer Films"
IMR Advisory Panel
I. C. Sanchez
Spring, 1978

"Statistical Thermodynamics of Polymer Solutions"
University of Minnesota, Chemical Engineering Department, Minneapolis,
Minnesota
I. C. Sanchez
May, 1978

"Critical Behavior in Polymer Blends and Solutions"
Polymer Physics Gordon Conference, New Hampton, New Hampshire
I. C. Sanchez
June, 1978

"Critical Behavior in Polymer Blends and Solutions"
Xerox Corporation, Joseph Wilson Technical Laboratories, Rochester, NY
I. C. Sanchez
August, 1978

"Equilibrium Distribution of a Minor Constituent Between a Polymer and
Its Environment"
ACS National Meeting, Miami Beach, Florida
I. C. Sanchez
September, 1978

"Standardization of Gas Transmission Measurements"
Mid Atlantic Regional Meeting of ACS, Hunt Valley, MD
J. D. Barnes
April, 1978

"Assessing Permeation Performance of Industrial Plastic Shipping
Containers"
36th ANTEC Meeting of the Society of Plastics Engineers, Washington,
D.C.
J. D. Barnes
April, 1978

"Standardization of Gas Transmission Measurements"
American Chemical Society Symposium on Sorption and Transport in
Glassy Polymers, Miami Beach, Fla.
J. D. Barnes, and G. M. Martin
Sept., 1978

"Creep Failure and Fracture of Polyethylene in Uniaxial Extension"
ACS Meeting, Anaheim, CA
J. M. Crissman
March, 1978

"Lifetime Behavior of Polyethylene Bars in Uniaxial Extension in
Various Chemical Environments"
ACS Meeting, Miami, FL
J. M. Crissman
September, 1978

"An Instability Leading to Failure in Uniaxial Extension
ACS Meeting, Anaheim, CA
L. J. Zapas
March, 1978

"Stress-Strain-Time Diagrams, Including Failure Envelopes, for
High Density Polyethylenes of Different Molecular Weight"
ACS Meeting, Miami, FL
L. J. Zapas
September, 1978

"Nonlinear Viscoelastic behavior of PMMA in Torsion"
Massachusetts Institute of Technology
G. B. McKenna
June, 1978

"Enzyme-Enzyme Interactions on Steady-State Kinetics. Some Exact
Results in a One-Dimensional Lattice-Fluid Model"
NIH, Bethesda, MD
R. J. Rubin
May, 1978

"The Nature of the Glass Transition"
University of Illinois, Urbana, IL
E. A. DiMarzio
April, 1978

"Nonlinear Viscoelastic Behavior of Poly(methyl methacrylate) in Torsion"
University of Utah, Salt Lake City, Utah
G. B. McKenna and L. J. Zapas
February, 1978

"Brownian Motion, Polymer Chain Adsorption, and Interacting Enzymes"
NIH, Bethesda, MD
R. J. Rubin
November, 1977

"Solid-State ^{13}C NMR in Polyethylene: A quest for Molecular Insights in a Strongly Coupled System"
Denver, Colorado
D. L. Vanderhart
August, 1978

"Polymers At Surfaces"
University of MD, College Park, MD
E. A. DiMarzio
March, 1978

"Counting Statistics for Polymers"
University of Illinois, Urbana, IL
E. A. DiMarzio
March, 1978

"Degradation Kinetics Applied to Lifetime Predictions of Polymers"
17th Annual Meeting, Eastern Analytical Sym., New York, NY
J. H. Flynn
November, 1977

"Degradation Kinetics Applied to Lifetime Prediction of Polymers"
Delaware Valley Thermal Analysis Group Meeting, Media, Pennsylvania
J. H. Flynn
March, 1978

"Thermal Degradation of Polyurethanes"
Naval Research Labs., Washington, D. C.
Brian Dickens, and Leslie E. Smith
March, 1978

"Application of New Kinetic Techniques to the Lifetime Prediction of Polymers"
ACS Meeting, Miami Beach, Florida
J. H. Flynn and Brian Dickens
Sept., 1978

"Degradation Kinetics Applied to Lifetime Prediction of Polymers"
2nd International Symposium on Degradation and Stabilization of
Polymers at Dubrovnik, Yugoslavia
J. H. Flynn, and Brian Dickens
October, 1978

"New Techniques of Kinetic Analysis Applied to Polymer Degradation
Reactions"
U. of Glasgow, Glasgow, Scotland
J. H. Flynn
October, 1978

"Translational Diffusion and Polydispersity of Polystyrene at Theta-
Condition Studied by Quasielastic Light Scattering"
University of Wisconsin
C. Han
November, 1977

"Neutron Scattering from Rubber Networks"
Sandia Laboratories
C. Han
March, 1978

"Small Angle Neutron Scattering of Polymers"
Navy Polymer Characterization Meeting
C. Han
March, 1978

"A Historical Perspective"
IADR/AADr Symposium, Washington, DC
G. C. Paffenbarger
March, 1978

"The Components in Composite Restorations"
IADR/AADR Symposium, Washington, DC
R. L. Bowen
March, 1978

"Physical and Chemical Properties and Wear"
IADR/AADR Symposium, Washington, DC
George Dickson
March 1978

"Clinical Placement and Performance"
IADR/AADR Symposium, Washington, DC
N. W. Rupp
March, 1978

"Biomaterials in Dentistry"
Johns Hopkins University, Baltimore, MD
N. W. Rupp
February, 1978

"The Selection and Use of Dental Materials by the General Dentist"
Ohio State University and the Scranton Dental Society
N. W. Rupp
February, 1978

"The Chemistry of Adhesive Bonding in Orthodontics"
The University of Pennsylvania, Centennial Orthodontic Program
R. L. Bowen
April, 1978

"Dental Composites"
University of Virginia and National Naval Dental Center, Bethesda MD
R. L. Bowen
April, 1978

"Dental Materials"
Department of Operative Dentistry, Catholic University, Nijmegan,
The Netherlands
N. W. Rupp
June, 1978

"Opportunities for Piezoelectric Polymer Sensors in Industry"
Lord Corporation, Erie, Pennsylvania
S. Edelman
April, 1978

"Piezoelectric Polymer Transducers for Communication"
J.M.R. Systems Corporation, Salem, NH
S. Edelman
July, 1978

"Dipolar Phenomena in PVF_2"
IBM, San Jose. California
M. G. Broadhurst
March, 1978

"Non-Linear Effects in Polymers"
Dielectric Gordon Research Conference, Plymouth, NH
M. G. Broadhurst
July, 1978

"Piezoelectricity and Pyroelectricity in Polyvinylidene Fluoride"
ONR, Meeting on Piezoelectric Polymers
M. G. Broadhurst
June, 1978

"Order-Disorder Transitons in Polytetrafluoraethylene: Theory and Effort on Properties"
Caracas, Venezuela
R. K. Eby
January 19, 1978

"Order-Transitions in Polytetrafluoraethylene"
Johns Hopkins Univ. Baltimore, MD
R. K. Eby
February 15, 1978

"Progress in Piezoelectric Polymers"
ONR, Polymer Conference, USNA, Annapolis, MD
M. G. Broadhurst
June, 1978

"Piezoelectricity and Pyroelectricity in Polymers"
Macromolecular Science Colloquia, Case Western Reserve University
G. T. Davis
March, 1978

"Piezoelectricity in PVDF"
APS, Washington, D.C.
G. T. Davis
March, 1978

"Survey of Organic Piezoelectric Materials"
ONR-NRL Symposium on Electroactive Polymers, NRL, Washington, D. C.
G. T. Davis
August, 1978

"Measurement of Polydispersity of Narrow Fractions and Column Spreading by Recycle Size Exclusion Chromatography"
ACS, Miami Beach, FL
Herman L. Wagner
Sept. 15, 1978

"Lattice Model Studies of the Nematic-Isotropic Transition in Chain Molecules"
NIH, Bethesda, MD
Dr. F. Dowell
June 29, 1978

"Defect Motion which Transports Polyethylene Molecules Along the Chain Axis"
Gordon Conference on Polymer Physics, New Hampshire
Dr. D. H. Reneker
June 20, 1978

"Quasielastic Scattering by Polymer Solutions"
Gordon Conference on Polymer Physics, New Hampshire
Dr. C. C. Han
June 20, 1978

"Behavior of Dental Amalgam and Its Phases in Physical Measurements
and Clinical Investigations"
Freie Universitat, Berlin. W. Germany
Dr. N. W. Rupp
July 4, 1978

"Recent Developments in Composites and Dental Amalgam"
Catholic University, Nijmegen, The Netherlands
Dr. N. W. Rupp
June 22, 1978

"Measurement of Adsorbed Polymer Conformation"
Kyoto University, Japan
Dr. L. E. Smith
May 29, 1978

"Liquid Crystal Nematic-Isotropic Transition in Lattice Model with LJ
Pairwise Segmental Intermolecular Potentials"
39th Semi-annual Statistical Mechanics Meeting, Rutgers University
Dr. F. Dowell
May 19, 1978

"Lattice Model STudies of Chain Molecules at an Orientational Order-
Disorder Transition"
Bell Laboratories, Murray Hill, NJ
Dr. F. Dowell
May 17, 1978

"Effect of Enzyme-Enzyme Interactions on Steady-State Kinetics. Some
Exact Results in a One-Dimensional Lattice-Fluid Model"
NIH, Bethesda, MD
Dr. R. J. Rubin

"Degradation Resistance of Some Candidate Composite Biomaterials"
Tenth International Biomaterials Symposium
Dr. G. B. McKenna
April 29, 1978

"Defect Motion in Polyethylene"
Materials Science Seminar, Johns Hopkins University
Dr. D. H. Reneker
April 12, 1978

"Methyl Branches in Hydrocarbon Crystals"
APS meeting, Shorham-Americana
Dr. R. K. Eby
March 30, 1978

"Acoustic Emission Monitoring During Uniaxial Tensile Elongation of
Glass-Epoxy Composites"
APS meeting, Washington, D. C.
Dr. R. E. Green
March 30, 1978

"X-ray Topography of Large Diacetylene Single Crystals"
APS meeting, Washington, D. C.
Robert E. Green, Jr.
March 30, 1978

"Dynamics of a Polymer Attached to a Surface"
APS meeting, Washington, D. C.
Dr. E. A. DiMarzio
March 30, 1978

"Identification of Extended Forms of n-Alkanes in the Liquid State
by Raman Spectroscopy"
APS meeting, Washington, D. C.
Dr. B. M. Fanconi
March 30, 1978

"Creep Failure in Uniaxial Extension of Linear Polyethylene"
APS meeting, Washington, D.C.
Dr. J. M. Crissman
March 30, 1978

"Low Temperature Dielectric Loss Characteristics of Polypropylene"
APS meeting, Washington, D. C.
F. I. Mopsik
March 30, 1978

"Normal Force Response of PMMA"
APS meeting, Washington, D. C.
Dr. G. B. McKenna
March 30, 1978

"Soft Repulsive Potentials in a Lattice Model for Oriented Chain Molecules"
APS meeting, Washington, D. C.
Dr. F. Dowell
March 30, 1978

"An Infrared Study of Sorption'Desorption in Polymeric Films
APS meeting, Washington, D. C.
Joseph C. Phillips
March 30, 1978

"Plasma Poling of PVDF"
APS meeting, Washington, D. C.
Dr. G. T. Davis
March 30, 1978

"Straight Chain Segment Length Distribution of Annealed Polyethylene Crystals"
APS Meeting Washington, D. C.
March 29, 1978

"Effects of Thermally Generated Disorder on Intensity of Vibrational Spectra of Solid Polyethylene"
APS meeting, Washington, D. C.
J. Mazur, J. P. Colson, B. Fanconi and D. H. Reneker
March 29, 1978

"Conductivity Effects in Poling PVDF"
APS Meeting, Washington, D. C.
Dr. A. S. DeReggi
March 29, 1978

"Piezo- and Pyroelectricity in Poly(vinylidene fluoride) from Plasma Poling"
ACS Meeting, Anaheim, CA
J. E. McKinney
March 14, 1978

"Creep Failure and Fracture of Polyethylene in Uniaxial Extension"
ACS, Anaheim, CA
J. M. Crissman, and L. J. Zapas
March 13, 1978

"An Instability Leading to Failure of Polyethylene in Uniaxial Creep"
ACS meeting, Anaheim, CA
L. J. Zapas, and J. M. Crissman
March 13, 1978

"The Conformation of Adsorbed Polymers"
Society of Polymer Science Annual Meeting, Japan
Dr. Leslie. E. Smith
May 24-26, 1978

"Synthesis of a Polyfunctional Surface-Active Comonomer"
International Assoc. for Dental Res., Washington, D. C.
R. L. Bowen
March 18, 1978

"Reactivity of Amine Polymerization Accelerators at low Concentrations
under Aerobic Conditions"
International Assoc. for Dental. Res., Washington, D. C.
H. Argentar & R. L. Bowen
March 18, 1978

"Hydrolysis of $CaHPO_4 \cdot 2H_2O$ (DCPD) in the presence or absence of CaF_2"
International Assoc. for Dental Res., Washington, D. C.
M. S. Tung
March 18, 1978

"High Copper Content Dental Amalgam: Linear Dimensional Change after
Starage in Air for 65 Weeks at 60, 37 and 23 °C"
International Assoc. for Dental Res., Washington, D. C.
G. C. Paffenbarger
March 18, 1978

"Phosphate Ion Hydration: Crystal Structure of $Mg_3(PO_4)2.22H_2$ "
International Assoc. for Dental Res., Washington, D. C.
Dr. M. Mathew
March 16, 1978

"Production of a Cast Titanium-Base Partial Denture"
International Assoc. for Dental Res.,
R. M. Waterstrat
March 18, 1978

"The Selection and Use of Dental Materials by the General Dentist"
Scranton Dental Society, Scranton, PA
Dr. N. W. Rupp
March 22, 1978

"Biomaterials in Dentistry"
Johns Hopkins University, Baltimore, MD
Dr. Nelson W. Rupp
February 21, 1978

"Impressions and Dies"
Prince Georges County Hospital, Cheverly, MD
Dr. N. W. Rupp
March 30, 1978

"Dentistry with an Open Mind"
Minneapolis District Dental Society Meeting
Dr. N. W. Rupp
January 19, and 20, 1978

"Characteristics and Use of Various Direct Gold Materials"
Minneapolis Gold Foil Study Club, Minnesota
Dr. N. W. Rupp
January 19, 1978

"Amalgam, Cements and Esthetic Restorative Materials"
Massachusetts Dentla Society
Dr. N. W. Rupp
January 14, 1978

Technical, Professional and Standards Committee Participation and
Leadership

ISO, TC 150, Implants for Surgery
James M. Cassel
Chair, USA TAG

ASTM F4,20 Resources
ASTM F4 Medical and Surgical Materials and Devices
James M. Cassel
Member

MDSMB, ANSU, Medical Device Standards Management Board
James M. Cassel
Member

American National Standards Committee MD156
Mr. G. Dickson
Vice Chairman, (April, 1978)

NASC MD156, Restorative Materials
Dr. N. W. Rupp
Chairman

ANSC, Terminology and Special Projects
Mr. G. Dickson
Chairman (April, 1978)

ASTM F4 Medical and Surgical Materials and Devices
ASTM F4.20 Resources
Dr. G. M. Brauer
Chairman

ANSC MD 156
Dr. G. M. Brauer
Member

ANSC MD 156
Dr. R. L. Bowen
Member and Secretary Sub Committee - Toxicity Tests

AADR/IADR
Dr. W. E. Brown
Chairman, Tellers Committee

AADR/IADR
Dr. J. M. Cassel
Washington Section Delegate

AADR/IADR
Dr. J. M. Antonucci
Government Representative, Dental Materials Group

American Chemical Society
Dr. R. K. Eby
General Chairman, Macromolecular Secretariat Symposium

ASTM D-20 (Plastics)
Dr. R. K. Eby
Chairman

American Chemical Society
Dr. D. H. Reneker
Session Chairman, Macromolecular Secretariat Symposium

American Chemical Society
Dr. L. E. Smith
Session Chairman, Macromolecular Secretariat Symposium

Academy of Operative Dentistry
Dr. Nelson Rupp
President Elect and Program Chairman

AADR/IADR
Dr. G. M. Brauer
Program Chairman, 50 Anniv. Symposium

AADR/IADR
Dr. Nelson Rupp
Session Chairman

Acoustical Society of America
Mr. S. Edelman
Member

American Chemical Society
Dr. E. A. DiMarzio
PRF Advisory Panel

American Chemical Society
Dr. B. M. Fanconi
Session Chairperson

American Chemical Society
Dr. M. G. Broadhurst
Member

American Physical Society
Dr. F. A. Khoury
Session Chairperson

American Physical Society
Dr. E. A. DiMarzio
Vice Chairman, High Polymers Division
Prize Nominating Committee , High Polymer Physics Division
Session Chairperson

Intl. Association for Dental Research
Dr. W. E. Brown
Member

National Acad. of Engineering Conference on Electric Insulation and
Dielectric Phenomena
Dr. M. G. Broadhurst
Member

Technical Association of the Pulp and Paper Industry
Dr. E. L. Graminski
Member

Rheology Society of America
Mr. L. J. Zapas
Member, Executive Committee

American Association Dental Research
Dr. W. E. Brown
Member

Experimental NMR
Dr. D. L. Vanderhart
Board Member

Heat Capacity Measurements
Dr. S. S. Chang
Member

Electrical Standards Society
Mr. W. P. Harris
Member

Electrical Standards Society
Mr. C. G. Malmberg
Member

Electrical Standards Society
Mr. L. J. Zapas
Member

Electrical Standards Society
Dr. J. D. Barnes
Member

Plastics Standards Society
Mr. G. M. Martin
Member

Plastics Standards Society
Dr. J. C. Smith
Member

Plastics Standards Society
Dr. H. L. Wagner
Member

Plastics Standards Society
Mr. L. J. Zapas
Member

Thermal Standards Society
Dr. J. H. Flynn
Member

ASTM D-11 Rubber & Rubber-Like Materials
Dr. G. B. McKenna
Member

ASTM E-9 Fatigue
Dr. R. W. Denn
Member

ASTM D-2 Petroleum Products & Lubricants
L. J. Zapas
Member

International Electrotechnical Commission. Subcommittee TO46-WG3,
Polyethylene Insulation
Mr. L. J. Zapas
Member

ASTM Plastics D-20
Dr. J. D. Barnes
Member SC.12-Ethylene Plastics
        SC.19-Film and Sheeting
        SC.70-Measurement Techniques

ASTM Flexible Barrier Materials F-2
Dr. J. D. Barnes
Member Executive Committee
        SC.30-Measurement Methods

Implants for Surgery ISO/TC 150
Dr. R. K. Eby
Member

Medical Devices Technical Advisory Board
Dr. R. K. Eby
Member

ASTM Thermal Analysis E-37
Dr. J. H. Flynn
Member

ASTM Plastics D-20
Dr. D. H. Reneker
Member

ASTM Plastics D-20
Dr. H. L. Wagner
Member SC.70-Analytical Methods
        SC.04-Size Exclusion Chromatography
        SC.05-Molecular Weight Parameters (Chairman)

Flexible Barrier Materials F-2
Dr. D. H. Reneker
Member

Seminars for Staff and Guests

Dr. Steve Krause
"Important Deformation Mechanisms in Solid State Extruded Polyethylene"
December 19, 1977

Prof. Ziya Akcasu
"Concentration Dependence of Dynamic Structure Factor in Polymer Solution"
November 28, 1977

Dr. Robert Snyder
"Low Frequency Raman Spectroscopy and Structure of Polymer Molecules"
November 8, 1978

Dr. Robert Kusy
"Structure and Properties of Acrylic Polymers"
October 28, 1978

Dr. Robert Kusy
"Structure/Property Relationship Between Molecular Weight and Fracture Surface Energy in a Glassy Organic Polymer"
February 17, 1978

Dr. George Baran
"Phase Changes in Base Metal Alloys Along Metal Porcelain Interfaces"
April 20, 1978

Dr. R. A. Draughn
"Compressive Fatigue Limits of Dental Composite Restorative Materials"
April 27, 1978

Dr. J. A. Tesk
"Metal Ceramic Dental Systems, Today and Tomorrow"
May 5, 1978

Dr. Peter Moon
"Limitations of Dental Composite Resin Systems"
June 7, 1978

Dr. J. A. Tesk
"Effect of Gold Alloy Additions on Color"
June 2, 1978

Dr. Wen-li Wu
"Strain-Induced Crystallization Phenomena"
June 5, 1978

Dr. J. A. Tesk
"Stress Analysis and Dental Implant Performance"
July 5, 1978

Dr. P. Alexandrovich
"Phase Separation in Polymer Blends"
November 29, 1977

Prof. Akira Odajima
"Fine Structure of Polyoxymethylene Crystals Formed in Radiation-
Induced Solid State Polymerization"
November 2, 1978

Dr. C. J. Vonk
"Some Applications of Small Angle X-ray Scattering in Polymer Research"
October 17, 1977

Dr. J. A. von Fraunhofer
"Adhesive Dentistry"
October 3, 1977

Dr. Julia Higgins
"Possible Effects of Internal Flexibility on Dynamics of Long-chain
Molecules Observed by Neutron Scattering"
October 11, 1977

Dr. D. C. Bassett
"Characterization of Spherulitic Morphologies"
January 3, 1978

Dr. B. J. Briscoe
"The Friction and Wear of Polymers"
January 18, 1978

Prof. J. N. Sherwood
"Radiotracer Studies of Self-Diffusion Mechanisms in Organic Solids"
January 16, 1978

Prof. K. L. DeVries
"Evaluation of Adhesive Strength"
February 16, 1978

Dr. P. H. Lindenmeyer
"Small System Thermodynamics & Nucleation Theory
February 24, 1978

Dr. C. T. Levett
"A High Density Polyethylene Manufacturing Process and Quality Control"
March 1, 1978

Dr. R. L. Ayres
"Molecular Parameter-Property Relationships of High Density Polyethylene"
March 1, 1978

Prof. E. Fukada
"Piezoelectricity and Pyroelectricity of Polyvinylidene Fluoride"
March 31, 1978

Dr. N. Koizumi
"Dielectric Measurements in mHz Regions"
March 23, 1978

Prof. Richard J. Gaylord
"A new Approach to the Deformation of Bulk Polymers"
March 22, 1978

Dr. G. Davier
"Mechanical Properties of Highly Oriented Polyethylene"
March 12, 1978

Dr. C. P. Wen
"Improved Membrane Separation by Selective Chelation of Metal Ions in Aqueous Feeds"
April 13, 1978

Dr. P. E. Reed
"Dynamic Response and Fracture of Polymeric Systems on Impact Loading"
March 24, 1978

Dr. John Crowther
"Molecular Characterization of Polyolefins Using High Temperature GPC"
April 10, 1978

Dr. T. Nagasawa
"Processing of Plastics In Film"
April 27, 1978

Dr. T. Lohman
"The Effects of Salt Concentration on Protein Nucleic Acid Equilbria"
April 24, 1978

Dr. G. Senich
"Dynamic Mechanical Study of Phase Segregation in Polyurethanes"
April 21, 1978

Dr. C. G'Sell
"Determination of the Flow Curve of Rigid Polymers at Constant True Strain Rates"
April 21, 1978

Prof. J. M. Schultz
"In Situ Studies of Polyethylene Crystallization Using Oak Ridge 10 Meter Small Angle X-Ray Scattering Facility"
May 25, 1978

Dr. J. R. Bishop,
"The Need for More Meaningful Extraction Testing Procedures"
May 17, 1978

Prof. Allegra
"Chain Folding in Polymer Crystallization"
June 8, 1978

Dr. A. Dilks
"The Application of ESCA to Investigations of Surface Modifications of
Polymers, Induced by Plasma Techniques"
September 6, 1978

Prof. B. H. Zimm
"Fast Internal Motions of the DNA Molecule"
June 6, 1978

Dr. C.E.R. Jones
"Analytical Pyrolysis"
May 23, 1978

Dr. N. Bikales
"Polymer Research Viewed from the National Science Foundation"
May 24, 1978

Dr. Michael Kashtock
"Use of Inverse Phase Gas Chromatography for the Study of Thermodynamic
and Morphological Properties of Polymers"
June 13, 1978

Dr. F. W. Wiegel
"Flow of a Fluid Through a Macromolecular Coil"
July 6, 1978

Dr. G. Williams
"Dielectric and Dynamic Kerr-effect Studies of Molecular Motion"
August 3, 1978

Dr. Claudine Williams
"Polyelectrolytes: A Small Angle Neutron Scattering Study of Semi-
dilute Solutions"
June 28, 1978

Dr. C. V. Jannink
"Polymers in Dilute and Semidilute Solution"
July 5, 1978

Prof. S. Penczek
"Progress in the Polymerization of Cyclic Acetals"
July 24, 1978

Dr. Wen-li Wu
"Research on Mechanical Properties of Dental Composite Restoratives"
July 7, 1978

Dr. M. Feughelman
"Dynamic Loss and Dynamic Modulus Measurements in Keratin Fibers an
Their Relationship to Molecular Structure"
June 30, 1978

Dr. D. Katz
"Rheology of Densely Cross-linked Polymeric System Subjected to Aging
under Stress"
August 16, 1978

Prof. G. Chu
"Static and Dynamic Properties of Polymer Solution in Dilute and Semi-
dilute Region"
August 18, 1978

Dr. A. J. Cobbold
"The Application of Microscopical Techniques to Industrial Polymer
Science"
August 10, 1978

Dr. E. Kroner
"Statistical concept of Stress and Microstructural Parameters of Paper"
July 28, 1978

Dr. J. R. Shelton
"Autooxidation and Stabilization of Polymers"
September 15, 1978

Dr. J. R. Scherer
"CH_2 Polymer Chain Length from Raman Spectroscopy"
August 28, 1978

Prof. Marian Kryszewski
"Electrical Properties of Polymers"
September 12, 1978

Dr. Sidney B. Lang
"Pyroelectricity: A 2300-Year History"
September 8, 1978

Dr. Sueo Kawabata
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